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Report No. CETHA-TS-CR-91076

**US Army Corps
of Engineers**

Toxic and Hazardous
Materials Agency

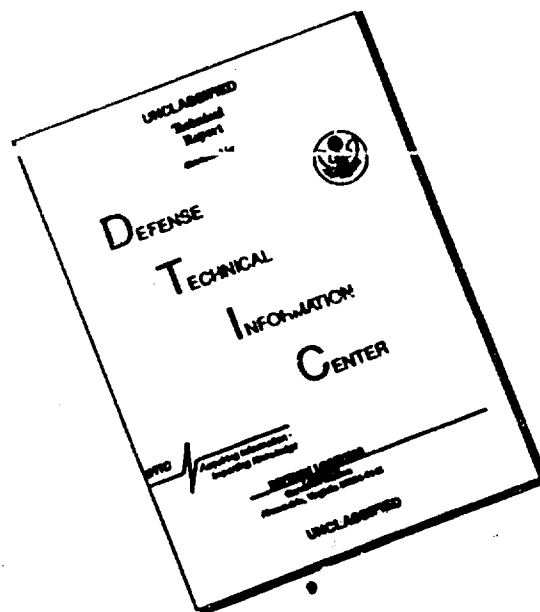
PROCEEDINGS FROM THE

**15th Annual Army
Environmental
R&D Symposium**

91-15380

25-27 June 1991
Williamsburg Hilton
and National Conference Center
Williamsburg, Virginia

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<p>Symposium conducted as a useful means of technology exchange for the Army's Environmental R&D Program. This annual event involves key personnel from all pertinent Federal agencies and provides a forum where users and developers are kept abreast of latest state-of-the-art technologies. This report provides proceedings from the symposium.</p>					
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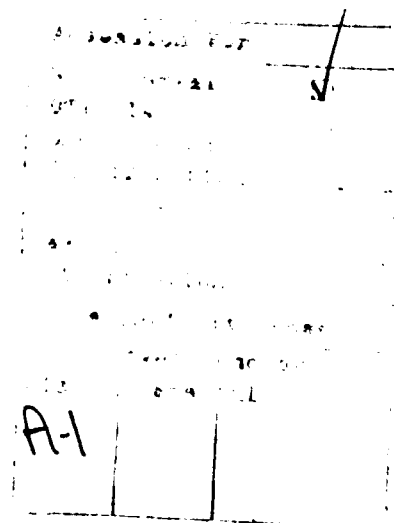
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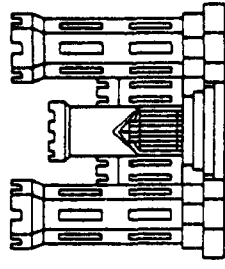
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15TH ANNUAL ARMY ENVIRONMENTAL R&D SYMPOSIUM

MG PETER J. OFFRINGA

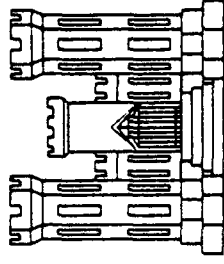
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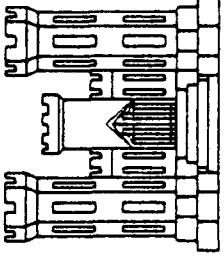


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WE HAVE A GREAT
CHALLENGE

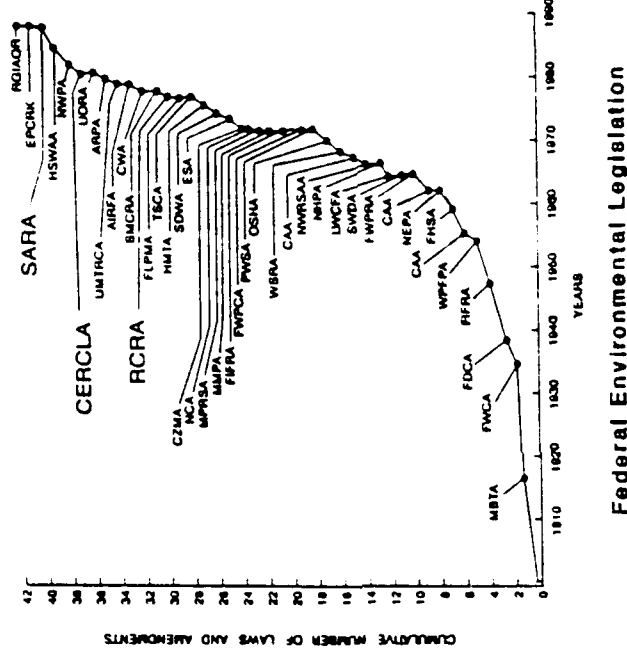


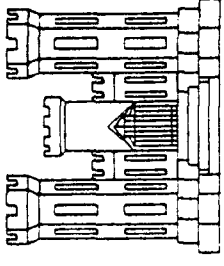
PROGRAM DRIVERS

- Regulatory mandate from EPA and states



- Increasingly stringent health standards
- Demand for analytical methodology to achieve detection and monitoring in ppb-ppt concentrations
- Emphasis on prevention to reduce future cleanup cost
- Increasing costs of environmental compliance

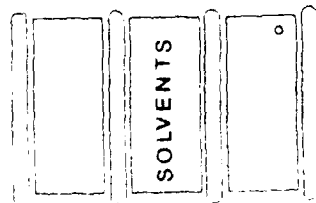
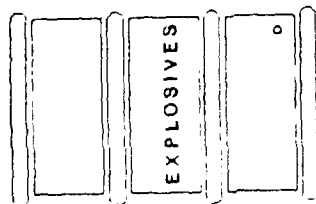
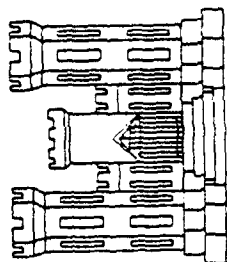




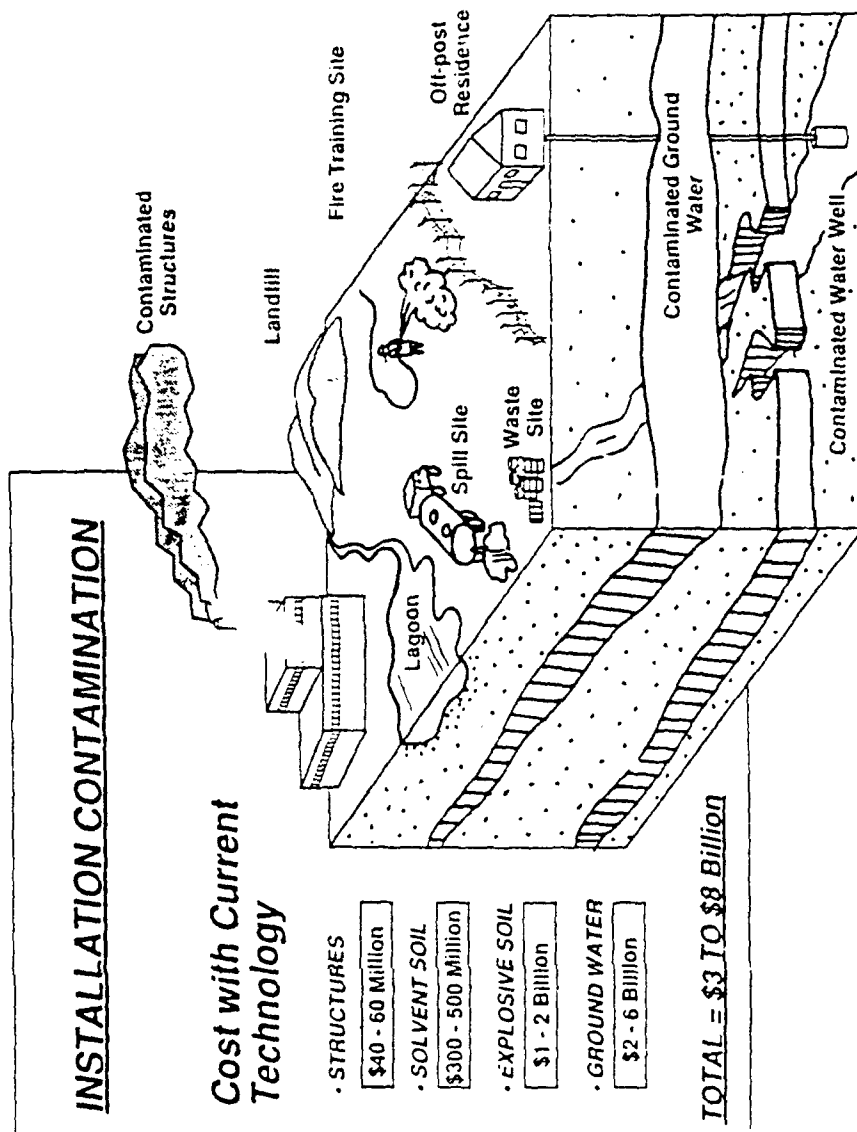
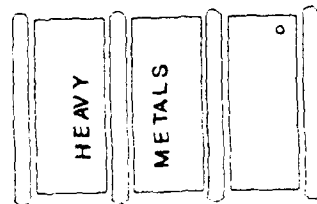
MAGNITUDE OF PROBLEM

- ✓ 17,482 DOD SITES
- ✓ 100,000+ TONS/YEAR OF HAZARDOUS WASTES
HAVE TO BE TREATED
- ✓ MILITARY UNIQUE COMPOUNDS
- ✓ LONG TERM LIABILITY
- ✓ REGULATORY COMPLIANCE - EPA\STATE\LOCAL
- ✓ COST: MULTI-BILLIONS OF DOLLARS -
DECADES OF TIME

HIGH COST OF CLEANUP

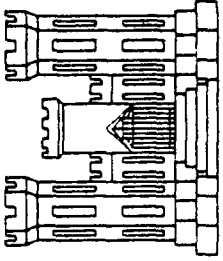


R&D COMPOST
PROCESS COULD
REDUCE COST
BY \$600 MILLION



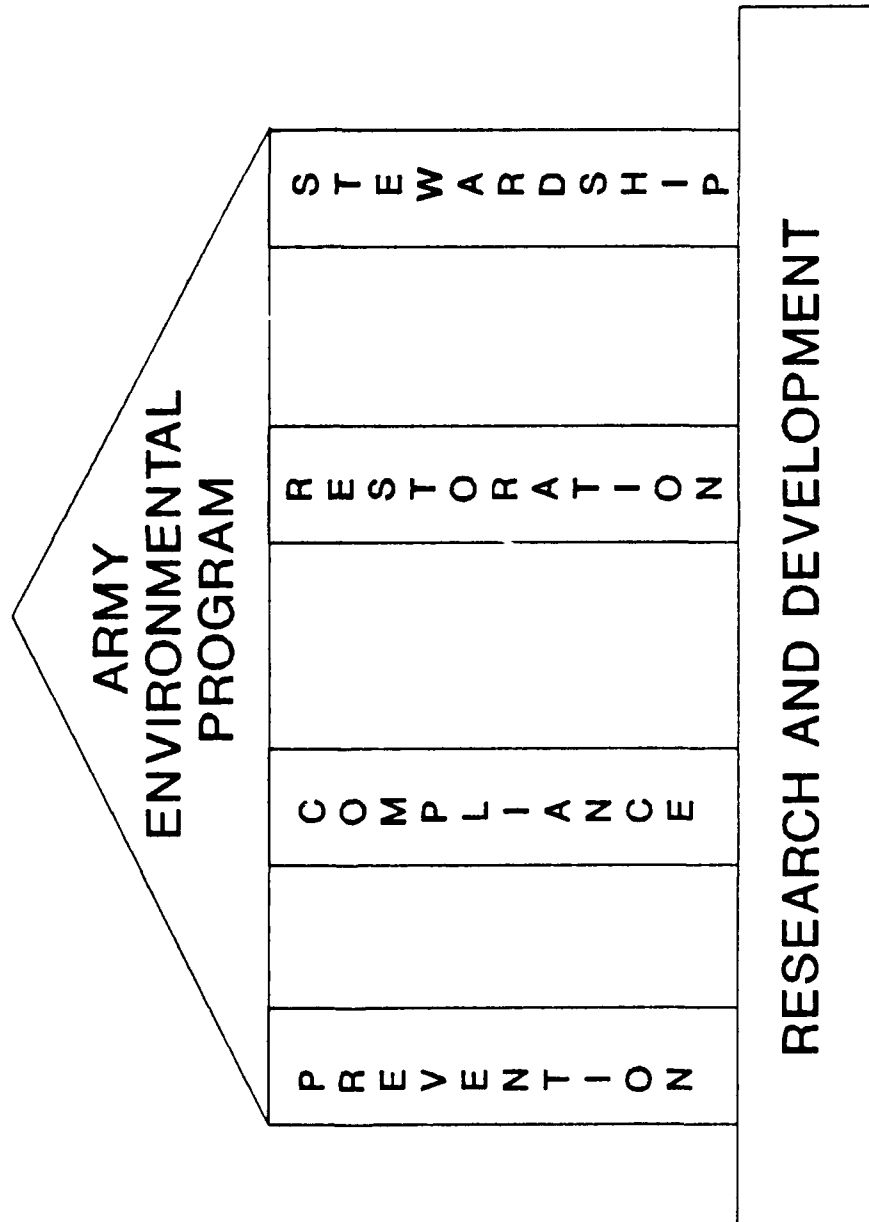
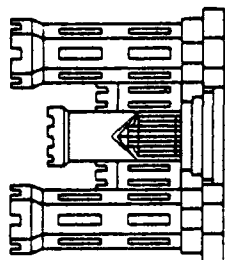


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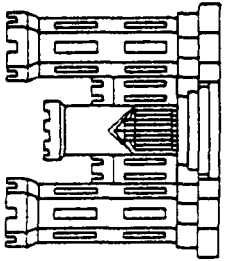
WE HAVE A GOOD PROGRAM

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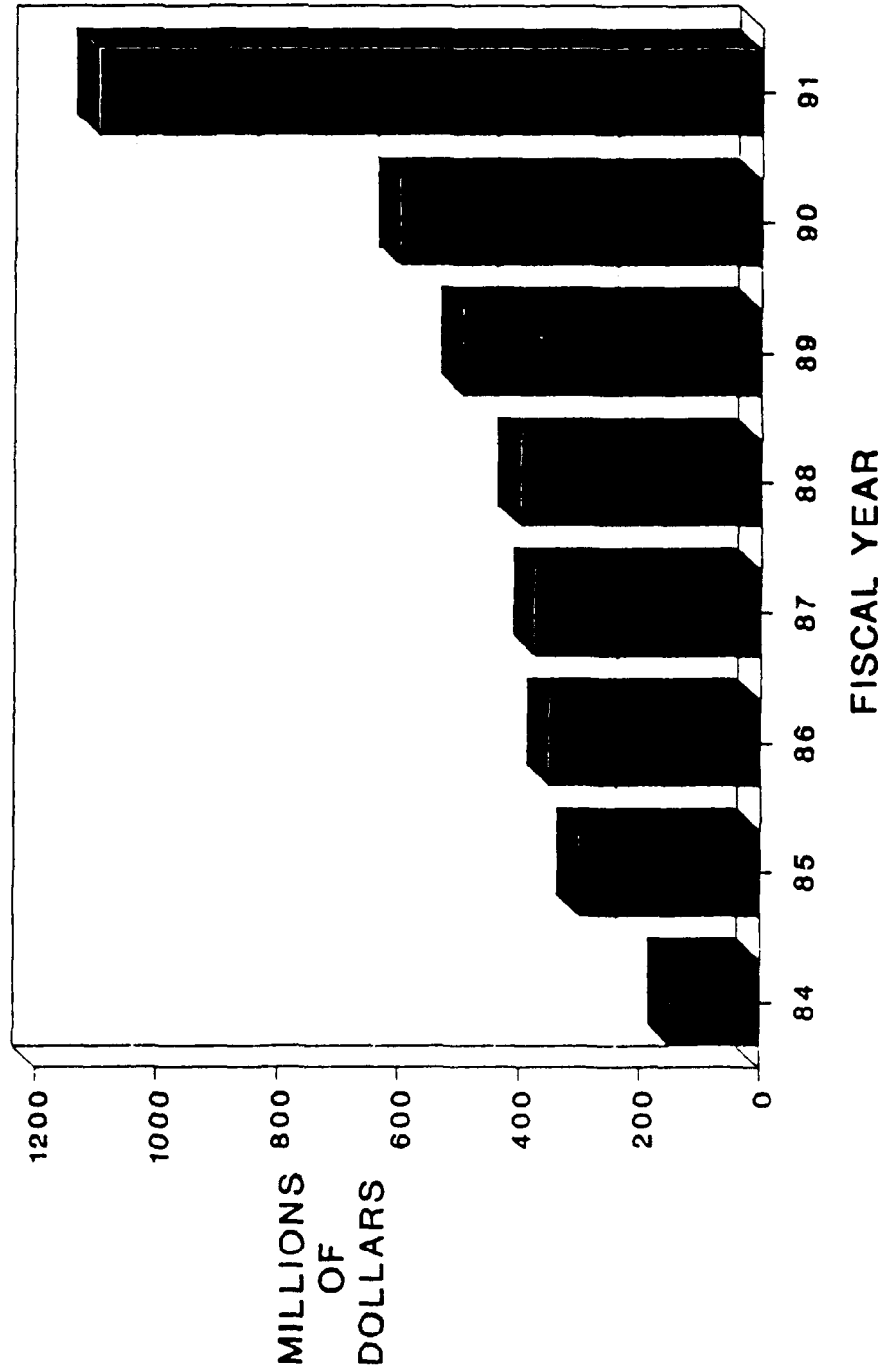




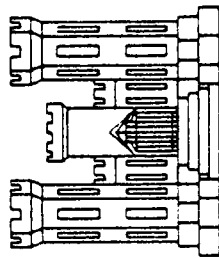
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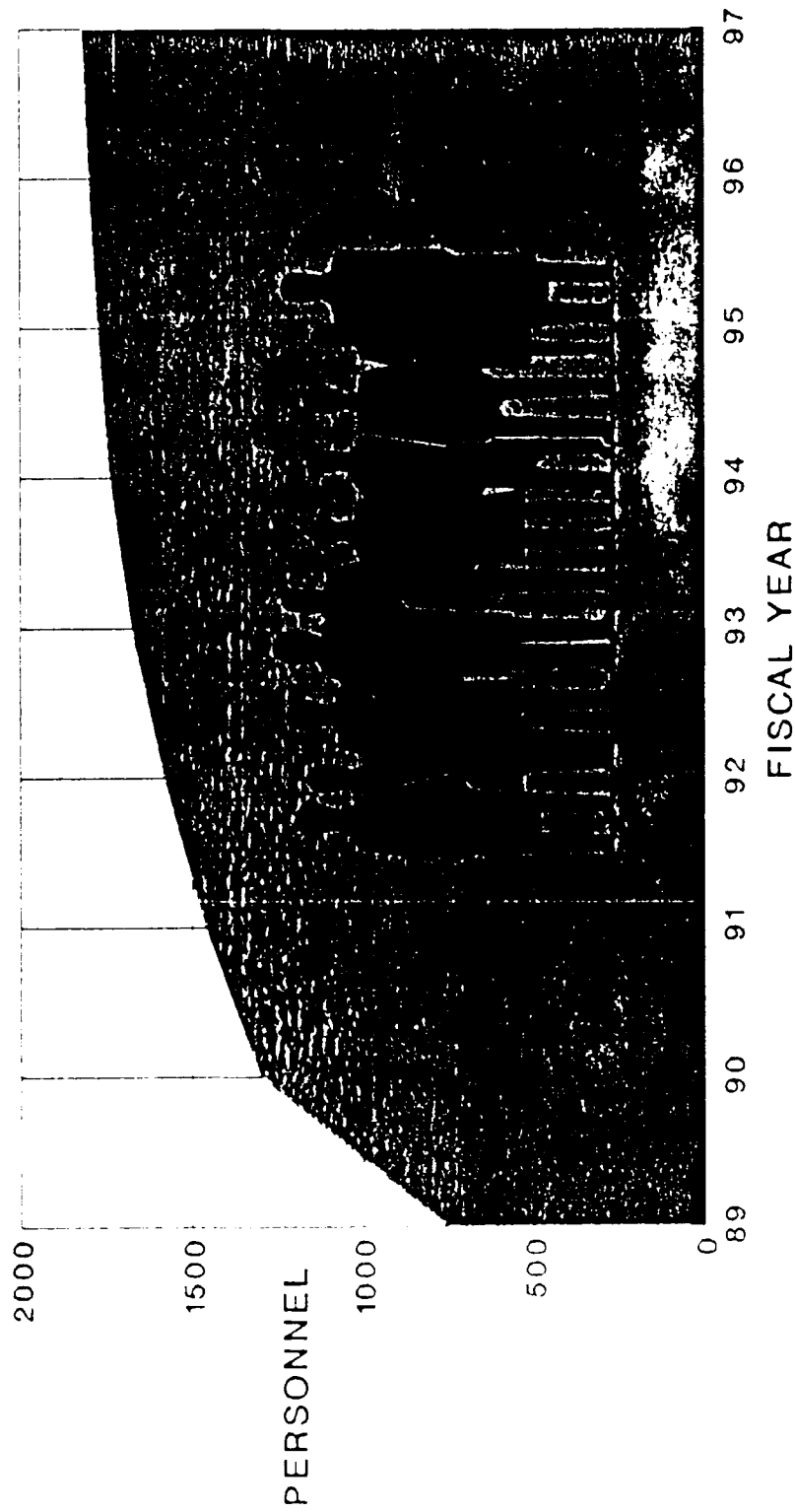
DEFENSE ENVIRONMENTAL RESTORATION PROGRAM FUNDING



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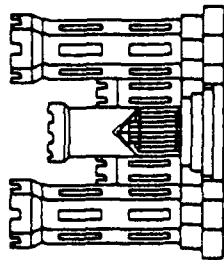


ENVIRONMENTAL STAFFING
TOTAL ARMY





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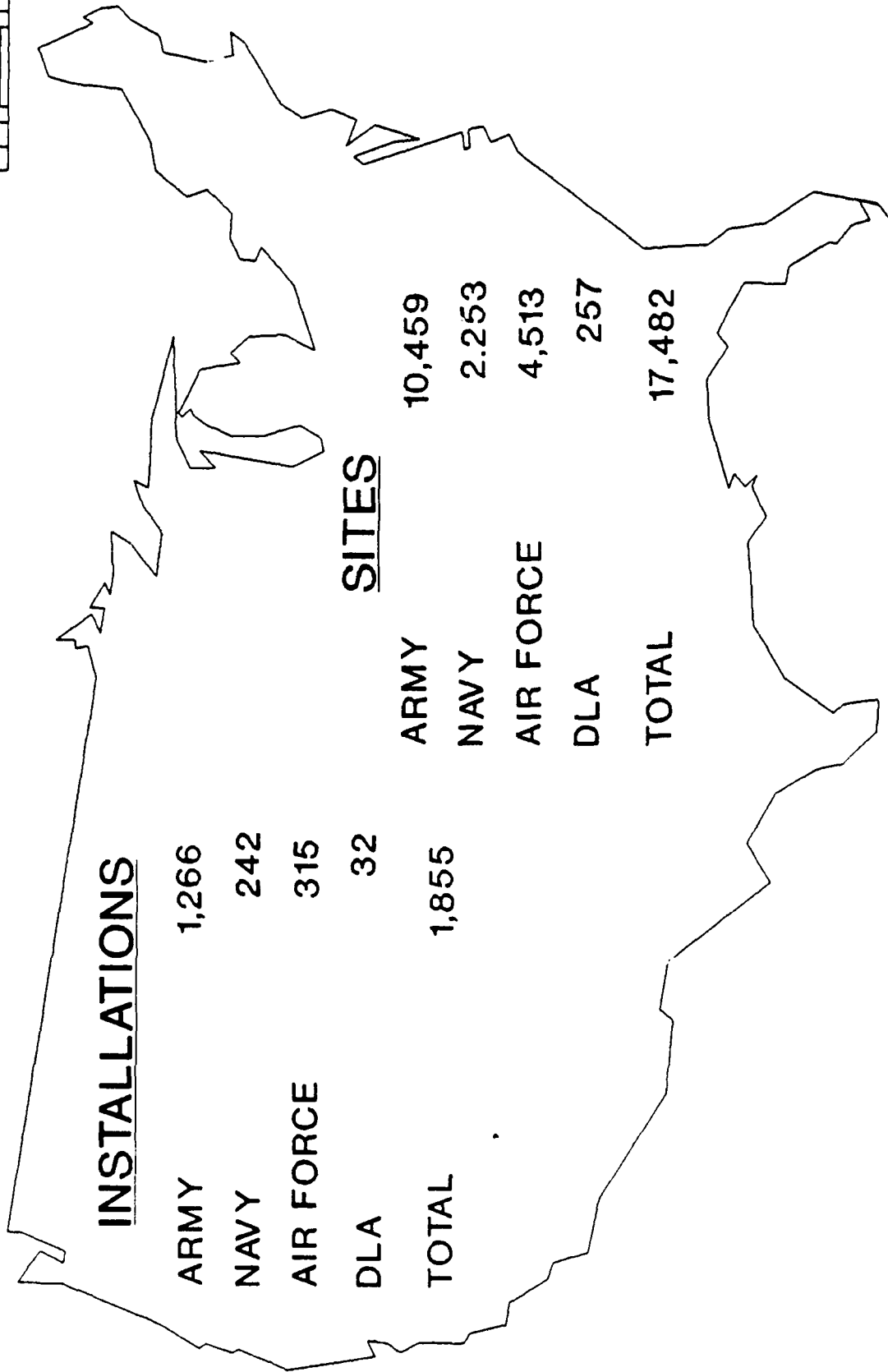


INSTALLATIONS

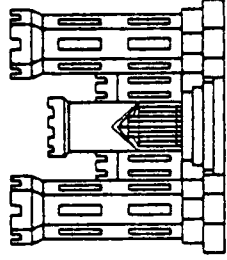
ARMY	1,266
NAVY	242
AIR FORCE	315
DLA	32
TOTAL	1,855

SITES

ARMY	10,459
NAVY	2,253
AIR FORCE	4,513
DLA	257
TOTAL	17,482



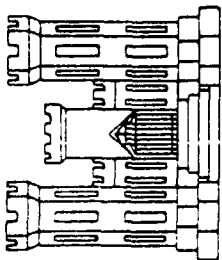
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R&D CAN MAKE US BETTER



U.S. ARMY CORPS OF ENGINEERS



GOAL



SUCCESSFUL ACCOMPLISHMENT OF
ENVIRONMENTAL RESEARCH & DEVELOPMENT

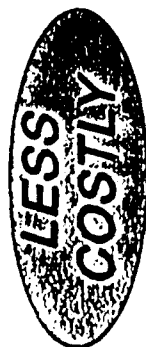


ENVIRONMENTAL CLEANUP AND
WASTE MANAGEMENT

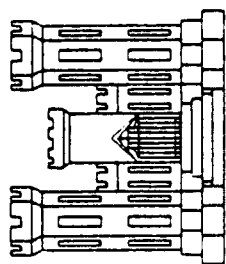


IMPROVED ARMY READINESS

WITH
PUBLIC
SUPPORT



TECHNOLOGY ADVANCEMENTS



In-Situ Biotreatment

Dig & Haul

Thermal Stripping



Composting

Incineration

In-Situ Air Stripping

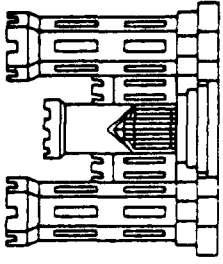
Down The Road

Containment



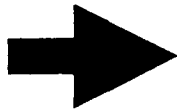


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BOTTOM LINE

WHY RESEARCH & DEVELOPMENT



- ✓ RESOURCE MULTIPLIER FOR SERVICES
- ✓ POTENTIAL USES OUTSIDE DOD
- ✓ DEMONSTRATION OF OUR COMMITMENT
- ✓ PREVENTION

**DEPARTMENT OF ENERGY
ENVIRONMENTAL RESTORATION TECHNOLOGY DEMONSTRATION PROGRAM
THE INTEGRATED DEMONSTRATION CONCEPT**

R. E. Adams
Hazardous Waste Remedial Actions Program *
Martin Marietta Energy Systems, Inc.
Department of Energy Demonstration, Testing, and Evaluation
Program Support Office
Oak Ridge, Tennessee 37831 (615-435-3115)

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Demonstration, Testing, and Evaluation Division
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Washington, DC 20545 (301-353-7295)

ABSTRACT

The Department of Energy's (DOE) Office of Technology Development is developing new and innovative environmental restoration technology through research, development, demonstration, testing, and evaluation. Technology development centers on solving environmental restoration problems common to many DOE sites. The concept of an integrated demonstration was developed to solve these problems. An integrated demonstration uses a timely and cost-effective management concept; through a multidimensional approach, interactive technologies for solving environmental restoration problems are assembled and evaluated at a common waste site to demonstrate their usefulness as a system. An integrated demonstration can be described in three dimensions: technology filtration, operational, and technology integration. The technology filtration dimension provides a technology assessment process that allows selection of the most promising new technologies from the innovative technology program; from the applied research and development program; and from technologies of industry, other governmental agencies, and foreign countries for each functional step of the operation. The operational dimension represents functional, programmatic steps necessary to solve an environmental cleanup problem end-to-end (e.g., from characterization through final monitoring for environmental restoration). During the integrated demonstrations, a systems approach is used to ensure efficiency, completeness, and compatibility with each step's operational requirements. The technology integration dimension facilitates the public's and regulatory bodies' quick acceptance of environmental restoration activities through the introduction of new technologies and by interactions with concerned individuals and organizations. A number of integrated demonstrations are ongoing, being initiated, or being planned at DOE sites. Several will be described to illustrate the manner in which an integrated demonstration functions.

* Hazardous Waste Remedial Actions Program, Oak Ridge, Tennessee 37831, managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.



1. INTRODUCTION

The Department of Energy (DOE) is committed to bringing its facilities and associated waste sites into compliance with national environmental laws within the next 30 years. This commitment will be accomplished through DOE's Office of Environmental Restoration and Waste Management (EM). EM is responsible for the management of waste from past, present, and future DOE nuclear programs and for the DOE sites that generate these wastes. The environmental problems are far ranging in technical scope and geographical distribution. Technical operations include addressing wastes generated during the past years of operation as well as current production at operating facilities. The wastes include radioactive materials, hazardous chemicals, and mixtures of both; these wastes are at DOE sites in more than 30 states. The Office of Technology Development within EM is responsible for developing new and innovative environmental restoration technology through research, development, demonstration, testing, and evaluation, which center on solving waste problems common to most DOE sites. To reach the 30-year goal, EM needs new and innovative technologies that achieve waste remediation in a faster, cheaper, better, and safer manner than those currently available. The concept of an integrated demonstration was developed to expedite the demonstration of these new and innovative technologies.

2. INTEGRATED DEMONSTRATIONS

An integrated demonstration is a time- and cost-effective management concept; through a multidimensional approach, interactive technologies for solving environmental restoration problems are assembled and evaluated at a common waste site to demonstrate their usefulness as a system. An integrated demonstration can be described in three dimensions: technology filtration, operational, and technology integration. The technology filtration dimension provides a technology assessment process that allows selection of the most promising new technologies from the innovative technology program; from the applied research and development program; and from technologies of industry, other governmental agencies, and foreign countries for each functional step of the operation. The operational dimension represents functional programmatic steps necessary to solve an environmental cleanup problem end-to-end (e.g., from characterization through final monitoring for environmental restoration). During the integrated demonstration, a systems approach is used to ensure efficiency, completeness, and compatibility with each step's operational requirements. The technology integration dimension facilitates the public's and regulatory bodies' quick acceptance of environmental restoration activities through the introduction of new technologies and by interactions with concerned individuals and organizations.

Demonstration, testing, and evaluation projects have been divided into three major areas: (1) Groundwater and Soils Cleanup, (2) Waste Retrieval and Waste Processing, and (3) Waste Minimization. Integrated demonstrations to investigate the priority issues of each area are ongoing, being initiated, or being planned at various DOE sites. Several integrated demonstrations in the groundwater and soils cleanup area and in the waste retrieval and waste processing area will be described to illustrate how an integrated demonstration functions.



2.1 GROUNDWATER AND SOILS CLEANUP

Contamination of soils and groundwater is one of DOE's most pervasive environmental restoration challenges. In the Eastern United States, where rainfall is more abundant than in the west, the precipitation has transported organic, radioactive, and heavy metal waste elements, causing contamination of the soil and of the groundwater usually found close to the land surface. The comparative aridity of the Western United States may reduce transport by the water mechanism there; however, wind erosion and unsaturated vapor transport pose equally challenging cleanup situations.

The integrated demonstrations organized in this category of environmental restoration are mobilized by the need to demonstrate cost-efficient, achievable means of cleaning up vast areas of contaminated soil and groundwater in the DOE weapons complex. The overall objective is to validate cleanup technologies for DOE implementation by demonstrating their effectiveness, cost savings ability, risk-reduction potential, and ability to reduce waste generation and improve DOE's capabilities to meet commitments, consistent with regulatory requirements and public acceptance.

The integrated demonstrations being implemented now are (1) Cleanup of Volatile Organics in Nonarid Soils and Groundwater, (2) Cleanup of Volatile Organics in Arid Soils and Groundwater, (3) Cleanup of Plutonium-Contaminated Surface Soils (arid site), and (4) Cleanup of Uranium-Contaminated Soils (nonarid site). The progress differs for each demonstration, depending its stage of development. The planning and implementation stages of each integrated demonstration are briefly described below.

2.1.1 Cleanup of Volatile Organics in Nonarid Soils and Groundwater

This integrated demonstration was DOE's first. Planning the demonstration was coordinated through the DOE Field Office, Savannah River, and began in October 1989. The initial objectives of this demonstration are to (1) develop, demonstrate, and compare technologies for remediation of volatile organics [e.g., trichloroethylene (TCE) and tetrachloroethylene (PCE)] in soils and groundwater; (2) span the cradle-to-grave requirements (e.g., from characterization and remediation to closure and monitoring); and (3) develop an integrated demonstration protocol as a basis for planning future integrated demonstrations. Directional drilling techniques (horizontal wells) are being used as are physical, chemical, and biological remediation technologies. This integrated demonstration also provides for the evaluation of an array of newly developed characterization and monitoring methods from across the DOE complex and private industry.

The remediation of volatile organics is one of DOE's top environmental issues. Implementation of new technologies for remediation, characterization, and monitoring should result in large cost reductions. Development costs can also be reduced by the integrated demonstration approach. The in situ cleanup technologies being developed for solvent contamination have applicability at other major DOE sites. Additionally, the characterization and monitoring technologies (e.g., fiber optic sensors and the cone penetrometer) can be used at many sites and may significantly reduce the costs of analytical sampling and monitoring well construction.

The demonstration's first phase involved evaluating an in situ air stripping process. Volatile contaminants (both TCE and PCE) were purged from the contaminated soil and groundwater by injecting air in a horizontal well installed below the contaminated aquifer and soil.



and extracted through a vacuum-extraction horizontal well installed in the vadose zone. The initial results show a consistent increase in volume over comparable operations with vertical wells and show maintenance of a substantial removal level through weeks of deployment. During the first field application, baseline characterization data on hydrogeology, geochemistry, and microbiology were accumulated, along with comparative data from coring techniques and monitoring well approaches (i.e., standard drilling and Hydropunch). In this integrated effort, standard monitoring techniques will be compared to new approaches in tomography and in situ groundwater flow measurements.

The next planned phase involves in situ bioremediation; indigenous microorganisms will be stimulated to degrade TCE, and directional drilling techniques will be used to deliver nutrients (principally methane) to the contaminated zone. Methane stimulates selected microbes (methanotrophs) that can degrade TCE. Surface bioreactor treatment of the contaminated off-gas and water will be coupled to the in situ remediation. Again, an extensive monitoring system will be used to evaluate the results of the biotreatment both in situ and aboveground. The development, demonstration, and evaluation of newly developed fiber optic detectors will also be monitored as will innovative sampling devices, regulatory requirements, and public acceptance.

Other plans for this integrated demonstration include demonstrating additional horizontal drilling techniques, innovative monitoring and characterization technologies, other in situ remediation techniques, and off-gas treatment systems.

2.1.2 Cleanup of Volatile Organics in Arid Soils and Groundwater

The objective of this integrated demonstration is to develop and compare technologies for removal and destruction of volatile organics (e.g., TCE and PCE) in arid sites. Additionally, in keeping with the integrated demonstration philosophy, the experience and lessons learned from the Savannah River nonarid site demonstration will be used. The integrated demonstration is expected to encompass all phases of remedial action, from site characterization and preliminary assessment through remediation and to evaluation of effectiveness and monitoring. Control and performance prediction methods must be applicable to arid zones or environments with large vadose zones. The integrated demonstration will survey and evaluate physical, chemical, thermal, biological, electrical, and mechanical technologies for characterization, remediation, and monitoring of contaminated soils and groundwater in arid environments. All regulatory and permitting requirements will be addressed as a prime segment of the demonstration.

Characterization technologies will concentrate on reducing costs and schedules for sampling and analysis and reducing disturbance of the sites. Remediation technologies will concentrate on the degradation of organics to innocuous commodities, such as carbon dioxide and water; elimination or reduction to permissible limits of chemical toxicity; extraction of chemical constituents for treatment; and stabilization and segregation of the contaminants from the biosphere. Remediation techniques will focus on reducing costs without creating ancillary waste streams. This demonstration is being held because of DOE's high level of concern for the environmental restoration of soils and groundwaters contaminated with organic solvents. Benefits of the demonstration arise from the applicability of these new technologies to priority cleanup needs at Richland, Idaho National Engineering Laboratory (INEL), Los Alamos National Laboratory, Pantex, Rocky Flats Plant (RFP), Lawrence Livermore National Laboratory, Sandia National Laboratories, other DOE sites, and other federal agencies (e.g., the National Aeronautics and Space Administration, Department of Defense).



The integrated demonstration will be conducted through the DOE Field Office, Richland, at a Hanford carbon tetrachloride (CCl_4) release site. The object of this integrated demonstration is to develop and compare technologies for the characterization, removal, and destruction of volatile organic constituents (e.g., CCl_4 , TCE, and PCE) at arid sites. Development and field validation of control and performance prediction methods applicable to arid climates or locales with large vadose zones are also vital considerations in the conduct of the integrated demonstration activities.

2.1.3 Cleanup of Plutonium-Contaminated Surface Soil

This integrated demonstration will initially concentrate on restoring one of the safety shot sites within the Nevada Test Site (NTS). Safety shot sites are typically contaminated on the surface with plutonium or uranium or both; typically 90 to 95% of the contamination resides in the top 5 cm of soil. In the cleanup operation, soil and vegetation will be removed selectively using techniques that reduce the volume of contaminated materials to be removed by possibly placing the coarser uncontaminated particles back on the original surface to serve as a protective cover, preventing wind erosion of the newly exposed surface. Revegetating the site to rehabilitate the fragile ecology of desert ecosystems will be studied. A gravimetric separation process was developed and tested at Johnston Atoll; the process achieved a 95 to 98% volume reduction of plutonium contaminated coral. Pilot equipment is now at NTS and is available for further evaluation and potential modification.

Other techniques, such as wet screening, magnetic separation, centrifugation, or hydrocycloning, may be evaluated depending on the soil type and the plutonium's physical characteristics. Limited studies of nuclear shots in NTS have shown that plutonium contamination is present in certain size fractions, mainly as fine plutonium (Pu) oxide particles. At RFP, investigations have shown that the Pu, though occurring as fine particles in the waste, has chemically aggregated into much larger granules than the initial particle sizes. These situations support the concept of integrated demonstrations, which would result in information useful for application at other NTS and DOE sites.

The contaminated soil particles removed from the surface must be disposed of so as not to create a new potentially hazardous site. Regulatory requirements will dictate the specific method to be used. While traditional methods, including cementation and impermeable cover, are being considered, advance techniques of in situ vitrification will also be explored.

One of the more difficult challenges may be restoring the cleaned site to its original ecosystem. Restoring vegetation to the soil in a harsh environment, with limited water and without the original surface, requires careful management. Removal of the surface soil exposes the less productive subsoil; the subsoil remaining is less permeable to water than the original surface, making the soil subject to erosion and compaction. In addition, young vegetation attracts wildlife, such as rabbits, and plants can be stripped of their tender leaves during the active growing season. EM is reviewing studies that have provided valuable information on the requirements for revegetation; effective methods to improve water infiltration, such as returning the coarse noncontaminated particles to the surface; and surface soil treatment to improve plant growth potentials.

All cleanup efforts must be followed with the deployment of a reliable monitoring system to establish successful remediation. The type of system used will depend on the requirements for cleanup levels and the techniques used. Thus, the combined and coordinated efforts of



characterization, cleanup with volume reduction, ultimate disposal of the contaminants, restoration of the site to a sound ecologic system, and documentation of the safe long-term cleanup of the contaminated site typify the integrated demonstration concept.

2.1.4 Cleanup of Uranium-Contaminated Soil

The objective of this integrated demonstration is to develop and demonstrate remediation methods for soils contaminated with uranium. The DOE Field Office, Oak Ridge, is coordinating the demonstration. Remediation techniques for cleaning up large areas contaminated with uranium will be evaluated for removal efficiency, economic feasibility, risk reduction, and waste minimization. Traditional methods for remediating radionuclide-contaminated soils, such as excavation, transportation, and permanent storage, are costly (estimates have been formulated of approximately \$700 or greater/yd³ depending on site and conditions) because of the large volumes of soil to be removed. The demonstration will span the cradle-to-grave phases involved in an actual cleanup, addressing all regulatory and permitting requirements and expediting future selection and implementation of the most appropriate technologies, in terms of immediate and long-term effectiveness, for all DOE sites. The demonstration will complement the demonstration for Pu contamination that the DOE Field Office, Nevada, is conducting at NTS.

The Feed Materials Production Center (FMPC), in Fernald, Ohio, is the site for the integrated demonstration of cleanup of uranium-contaminated soils because of its off-site contamination and because the state of Ohio's concerns are very pressing. Additionally, remediation technology information derived from the demonstration will be beneficial and may be transferred to the Oak Ridge, Portsmouth, Paducah, Idaho, Savannah River, and Richland sites for cleanup of radionuclide-contaminated soils. The primary problem at FMPC is that radioactive soil contamination, predominantly depleted uranium, is widespread.

The prospective demonstration site at FMPC is an area of contaminated soils adjacent to the solid waste incinerator, which is at the northwest corner of the sewage treatment plant. The incinerator was operated from November 1954 through December 1979 and was used to burn contaminated and uncontaminated burnable trash. Remediation for this site is important, because most of the contaminated soils are outside the fenced boundary of the sewage treatment plant, and a neighboring farmer has used the site through a lease agreement with DOE (i.e., DOE-owned land) to graze cattle. Remedial Investigation /Feasibility Study soil and core sampling data were collected; the highest concentrations of uranium were in the immediate vicinity of the incinerator, and the apparent plume extended toward the northeast, which is the most probable wind direction. Limited data from core samples for this area, down to 7 ft, show that uranium can penetrate the soil and may be adsorbed to the clay in the soils. The data also suggested that in some areas no remediation is necessary; other samples showed that remediation may be necessary in some areas down to 1 ft and in other areas down to 5 ft (probably because of fissure flow). In addition, physical cleanup techniques that may work in arid, sandy soils may not work well in the fine, clay soils at the FMPC site; the uranium is chemically exchanged on the soil at FMPC and does not appear in the discrete Pu particles found at the Nevada Pu demonstration site. FMPC will send soil samples to Nevada to determine the effectiveness of a gravimetric separation process (AWC process) for remediation of FMPC soils. Remediation techniques based on chemical removal (extraction) or desorbing radionuclides (uranium) from the soils may be required.



2.2 WASTE RETRIEVAL AND WASTE PROCESSING

In response to environmental mandates, waste retrieval and waste processing technologies will be developed and advanced through integrated demonstrations and other demonstrations that involve the following: (1) excavation or removal of contaminated material from the site or tank, by remote or direct contact techniques; (2) treatment and disposal of retrieved waste or waste arising from operations; (3) processing of contaminated material into a suitable form for shipping and/or disposal; or (4) decontaminating of materials, equipment, and decommissioning of facilities. These technologies will minimize the toxicity and volume of waste; accomplish faster, better, cheaper, and safer remediation of waste problems; and produce waste within regulatory guidelines for safe, permanent disposal.

A number of integrated demonstrations are under way or in the planning stages. They include buried waste, underground storage tanks, robotics, newly generated mixed waste, RCRA waste disposal, combustible waste treatment, in situ vitrification, decontamination and decommissioning of metal and concrete structures and materials, and advanced processing. Each integrated demonstration will use discriminating cradle-to-grave considerations to assemble, test, and evaluate related and synergistic technologies. These considerations will define an integrated system based on prototypic performance, safety, costs, and regulatory and social acceptability to remediate or manage DOE's environmental and waste management programs.

2.2.1 Buried Waste Integrated Demonstration

The buried waste integrated demonstration will focus on buried transuranic waste at INEL. The objective of this integrated demonstration will be to compare an array of technologies for in situ remediation and retrieval, separation and concentration, treatment, and disposal of mixed wastes from buried waste sites. The approach will span all phases involved in an actual cleanup and allow comparison to viewers to compare the technical performance of different available technologies under actual field conditions for potential use at other DOE facilities. Specifically, treatment technologies for radionuclides, toxic metals, and organic contaminants on rags, laboratory glassware, used test equipment, and other trash materials will be evaluated. Processing techniques to separate contaminants will also be demonstrated. The project is based on the need for improved separation and concentration technologies to separate mixed waste into its radioactive and hazardous components, allowing treatment and disposal consistent with EPA/NRC below regulatory control standards. The program is designed to contribute to meeting DOE/Idaho State commitment for RWMC remediation. Additional benefits include technology transfers to the Hanford, Los Alamos, Rocky Flats, Oak Ridge, and Savannah River installations.

2.2.2 Underground Storage Tanks Integrated Demonstration

The underground storage tanks integrated demonstration will focus on the Hanford waste tanks. The objective will be to identify, develop, test, evaluate, and transfer technologies required to remediate radioactive and mixed waste in underground storage tanks. The approach will span all phases involved in an actual cleanup and provide for technical performance comparisons of different technologies for potential use at other DOE facilities. Information on the reduction in operating exposures to radiation by use of new technologies (e.g., robotics) will be acquired. Tank remediation is one of the top three DOE cleanup issues. The 149 single shell tanks at the Hanford site are a primary concern. Success there will allow DOE to (1) meet Hanford's commitment to the state of Washington; (2) remediate underground storage tanks at other major

DOE production sites; and (3) transfer the technology to the FMPC to address silo problem and to the Savannah River and Oak Ridge installations to meet regulatory commitments.

2.2.3 Robotics

The Office of Technology Development plans to demonstrate robotic technologies in a wide variety of applications. The approach will span all hazardous phases involved in an actual cleanup and provide for technical performance comparisons of different available technologies. Potential applications to be demonstrated include remote sensing and characterization, underground storage tanks waste retrieval, other heavy waste removal operations, automated laboratory analysis, machining of plutonium and uranium components, and glovebox operations. The rationale for the program is the need to reduce the potential of personnel being exposed to hazardous and radiological materials and to conduct waste-generating and waste-handling operations better and less expensively. The benefits of this demonstration will be the comparison and evaluation of different technologies under actual field conditions for potential use at many DOE facilities.

3. CONCLUSIONS

These integrated demonstration activities will transfer new and improved waste remediation, waste retrieval and waste processing technologies to Environmental Restoration, Waste Operations, and Defense Programs where they will minimize the toxicity and volume of waste; manage unavoidable waste more efficiently and safely; accomplish faster, better, cheaper, and safer remediation of waste problems; effectively decontaminate materials and facilities; and produce waste within regulatory guidelines for safe, permanent disposal. New cleanup and waste management technologies must be continually developed, demonstrated, and implemented to achieve and maintain complete regulatory compliance.



"Construction, Testing, and Acceptance of Waste Covers for LLW and Uranium Mill Tailings"

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Background

By regulation, low-level radioactive waste (LLW) disposal facilities are required to achieve long-term stability on the order of 300 to 500 years (10 CFR Part 61.44). Uranium mill tailings must be controlled and disposed in a manner that will ensure stability for up to 1000 years to the extent reasonably achievable, and in any case, for at least 200 years (40 CFR Part 192.02). For both LLW and UMTRA wastes, emphasis in the regulations is on protection of public health and safety and protection of the environment from radiological and non-radiological hazards associated with the radioactive materials.

This paper summarizes recommendations made by the U.S. Army Engineer Waterways Experiment Station to the NRC for selection, placement, compaction, testing, and acceptance of soils for use in covers for LLW and uranium mill tailings wastes (Bennett et al., 1991). The guidance summarized in this paper addresses only soil cover components, specifically fine-grained soils for low-permeability or radon barrier layers and coarse-grained soils for filter and drainage layers.

Selection of Soils for Waste Covers

The basis used for evaluation of cover materials was a generally accepted group of cover functions with a regulatory basis, against which each Unified Soil Classification System (USCS) soil type was ranked according to its expected performance in that function. The cover functions were divided according to those that would be best satisfied by fine-grained soils (Table 1) and those best satisfied by coarse-grained soils (Table 2). Desirable characteristics of fine-grained and coarse-grained soils for waste covers are shown in Tables 3 and 4, respectively. A qualitative ranking system was used with preferred, acceptable, and unacceptable rankings assigned to each soil type for its performance of each function as shown in Tables 1 and 2. Some redundancy appears in the tables in both functional requirements and performance of the soils. Soil type recommendations by themselves were a convenient, but incomplete part of the overall approach to selection of soil layers used in cover systems. The rankings assigned to various soil types were justified on the basis of the desirable engineering properties and characteristics listed in Tables 3 and 4. Because some soils exhibit widely different properties and behavior, variable rankings were used in some cases to indicate the expected range of performance of these soils for particular functions. It could be argued that these cover functions do not address all the issues of concern in waste cover construction. Availability and transportation costs are important concerns. The ease or difficulty in



Table 1. Cover Functions and Rankings for Fine-Grained Soils Used for Low-Permeability Cover Layers
(P - Preferred, A - Acceptable, U - Unacceptable)

Soil Type	(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Minimize Infil- tration through Cover	Limit Dose Rate at Surface	Minimize Surface Erosion*	Minimize Diff. Settlement & Subsidence of the Cover	Minimize Dam. to Cover as Result of Diff. Set- tlement & Subsidence of wastes or under- lying material	Minimize Shrink/Swell Potential & Cracking	Provide Resistance to Freeze- Thaw
	P	P	A to U	A	A to U	A	A
Inorganic Clay (CL)							
Inorganic Highly Plastic Clay (CH)	P to U	P to U	A	A to U	A to U	A to U	A
Clayey Sand (SC)	P to U	P to U	A	P	P to U	P to A	A to U
Inorganic Silty Clay (CL-ML)	P to A	P to A	A to U	A	A to U	P for Shrink/Swell P to U for Cracking	A to U
Inorganic Highly Plastic Silt (MH)	A to U	A to U	A to U	A to U	A to U	A to U	U
Inorganic Silt (ML)	A to U	A to U	U	A	A to U	P for Shrink/Swell A to U for Cracking	U
Silty Sand (SM)	U	U	A to U	P	A to U	P	A to U

Highly Organic soils are not listed in this table, as they are deemed to be unsatisfactory for use as low permeability cover materials. However, they may be used for top soil layers to support vegetation.

* These materials should be protected through the use of riprap or vegetation. Unprotected fine-grained soils provide marginal to poor erosion resistance.

Table 2. Cover Functions for Coarse-Grained Soils Used as Drainage Cover Layers
(P - Preferred, A - Acceptable, U - Unacceptable)

Soil Type (USCS Class.)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Promote Drainage and Min. Contact of Water w/Wastes	Min. Surface Erosion	Min. Diff. Settle- ment & Subsid- ence of the cover	Min. Dam. to Cover from Diff. Settl. & Sub. of Wastes or Underlying Materials	Min. Shrink/ Swell Poten- tial	Dis- courage Burrowing	Min. Intru- sion (Root Pene- tration	Provide Resis- tance to Freeze/ Thaw
<u>Cobbles</u>	P	P	P	P	P	P	P	P
<u>Gravel</u>								
Well Graded (GW)	P	P	P	P	P	P	P	P
Poorly Graded (GP)	P	P	P	P	P	P	P	P
Silty Gravel (GM)	A to U	P to A	P to A	A to U	P	P to A	A to U	A
Clayey Gravel (GC)	U	P to A	P to A	A to U	P to A	P to A	A to U	A
<u>Sand</u>								
Well Graded (SW)	P to A	P	P	P	P	P to A	A	P
Poorly Graded (SP)	P to A	P to A	P	P	P	P to A	A	P
Silty Sand (SM)	U	A to U	P	A to U	P	A to U	A to U	A to U
Clayey Sand (SC)	U	A	P	A to U	P to A	A to U	A to U	A to U



Table 3. Desirable Characteristics of Low Permeability Soils for Waste Covers

Characteristic	Ratings			Comments
	Preferred	Acceptable	Undesirable	
USCS Soil Classification	CL	CH, SC, CL-ML	MH, ML, SM	Local availability impacts choices.
Plasticity Index (PI)	15 to 25	7 to 40	<7 >40	PI <7 or LL <20 may result in difficulty in meeting hyd. conductivity requirements. PI >40 or LL >70 may result in workability problems, i.e. hard when dry, sticky when wet, and difficult to adjust moisture content.
Liquid Limit (LL)	30 to 50	20 to 70	<20 >70	
Coarse Fraction:				
+1-in. size	None	≤3% by wt.	>3% by wt.	Larger percentages of coarse fraction may result in difficulty in meeting hyd. cond. criteria and may lead to damage of geomembranes if used. Max particle size must be much less than lift thickness.
+1/4-in. size	≤5% by wt.	5 to 10% by wt.	>10% by wt.	
Fine Fraction (% finer than No. 200 sieve size)	30 to 65%	15 to 100%	<15%	Fine fraction <15% may result in difficulty in meeting criteria for K. Fine fraction >85% may result in workability problems.
Hydraulic Conductivity (under expected long-term field conditions)	Dependent on project specific conditions		>1x10 ⁻⁷ cm/sec	Higher values of K could result in difficulty in satisfying long-term performance requirements.
Organic Material	None	<1% by wt.	>1% by wt.	Organic material increases hydraulic conductivity, compressibility and decreases long-term stability and shear strengths.
Shear Strengths	Dependent on project specific conditions			Minimum strength criteria must be based on site-specific considerations for stable slopes, adequate bearing capacity, limiting settlements and cracking.

Table 4. Desirable Characteristics of Filter and Drainage Soils for Waste Covers

Characteristic	Ratings			Comments
	Preferred	Acceptable	Undesirable	
USCS Soil Classification	For Drainage: Cobbles, GW, GP	SP, SW	GM, GC, SM, SC	Local climate, availability and location of layer within cover cross-section impact choices. For example, cobbles provide excellent drainage but are not satisfactory as filters. Hydraulic conductivity most important factor. Hydraulic conductivity value of drain should be at least approximately 10,000 times higher than hydraulic conductivity value of soil to be drained and high enough to quickly drain estimated infiltrating water w/large safety factor. Thickness is an important consideration for selecting minimum hydraulic conductivity of drain.
Hydraulic Conductivity	≥ 1 cm/sec	$> 1 \times 10^{-2}$ cm/sec	$< 1 \times 10^{-3}$ cm/sec	
Coarse Fraction				Physical and chemical stability more important than actual percentages of coarse fraction.
Fine Fraction (% finer than No. 200 sieve size)	<5%	<8%	>12%	Perm. greatly reduced by clay, silt, and even fine sand sizes.

* See NUREG/CR-5041 (Denson et al., 1987); Winterkorn and Fang, 1975; Bertram, 1940; Cedergren, 1967; and EM-1110-2-1901, 1986 for filter design criteria.



properly placing and compacting soils to achieve required performance is important. It is well known that highly plastic clays, and especially highly plastic silts are very difficult to work with. Adjustment of moisture contents and breaking up of large clods can be problematic with these soils. In addition the rankings for coarse-grained soils reflect their suitability for drainage, but do not explicitly judge performance as filter materials. Cobbles are obviously a poor choice as a filter but provide excellent drainage. Satisfaction of some functions depends not only on the soil type and its engineering properties, but to a large extent on its proper location, placement, thickness, slope, and characteristics of adjacent soils and other materials, including the wastes. In addition, some marginally satisfactory soils can be amended to improve their performance. These and other important concerns can be used to modify the overall rankings and soil selection criteria within the proposed evaluation system.

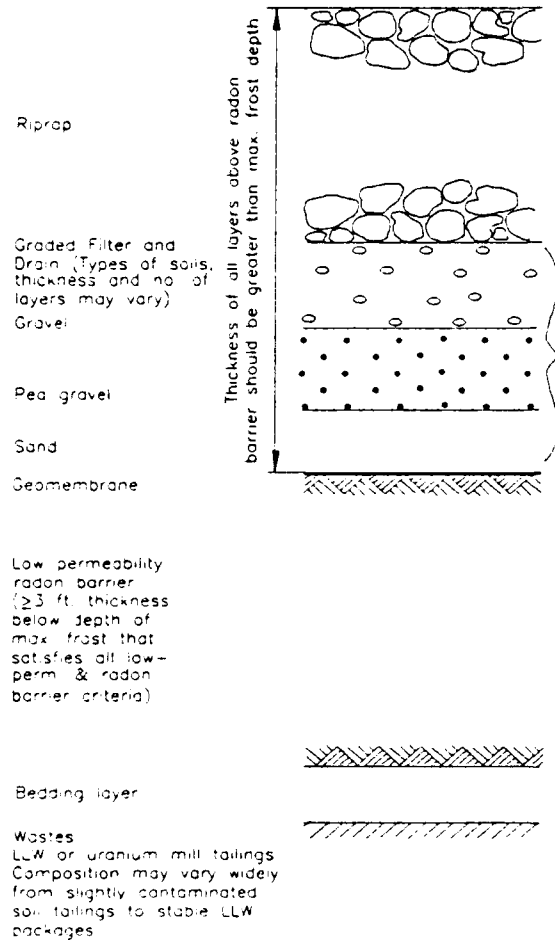
As shown in Table 1, for the evaluation and ranking system used, the preferred soil types for low-permeability cover layers would be inorganic clayey soils of medium plasticity that can be compacted to achieve a low hydraulic conductivity, and that would resist or be protected against damage from desiccation, cracking, heaving, erosion, settlement, and burrowing animals or root penetration for extensive periods of time. The soil types that would be considered suitable include the USCS classes CL, CH, SC, and CL-ML. Table 2 shows the most suitable soils for filter and drainage layers are the clean sands and gravels. Well-graded sands and gravels (SW and GW) are preferred for filter layers, while poorly graded sands (SP), gravels (GP), and cobbles would be expected to provide excellent drainage.

Because of the somewhat conflicting functional requirements imposed on a cover for these wastes, a multi-layer approach to cover design is recommended in which one layer complements and improves the performance of adjacent material layers and the entire cover. This approach allows the designer some flexibility in satisfaction of the conflicting requirements and avoids total reliance on any one material type or cover feature. Disadvantages of a multi-layer cover system in some cases may include higher material and construction costs due to limited availability of acceptable materials and added complexity in design, construction, and acceptance testing methods required to achieve desired results. In most cases, the positive attributes of the multi-layer soil cover system can be shown to outweigh the disadvantages. In Figures 1 and 2, multi-layered cover system conceptual designs are shown that should be capable of long-term satisfactory performance of the various cover functions. The conceptual designs differ primarily in the selection of the uppermost layer for protection of the underlying layers from erosion, freeze-thaw, and biointrusion.

Laboratory and Field Tests to Evaluate Soil Characteristics and Cover Performance

After the initial selection of soil types, properties, and engineering characteristics required to satisfy cover functions, the next concern is how to ensure that the borrow soils meet the selection criteria and that the cover, as constructed, satisfies all cover functions. A wide variety of laboratory and field test methods from simple index tests to elaborate full scale infiltration tests are available for this purpose. The key task is to clearly identify the characteristics and properties that are critical to

COMPOSITION



PURPOSE

Protects underlying low-perm. layer or radon barrier against erosion, freezing, desiccation, biointrusion (plant and animal)

Minimizes potential for standing head of water above low-perm. layer & provides additional protection against erosion, freezing, desiccation, biointrusion & radon escape. Should be sloped to provide drainage away from wastes

Minimizes potential moisture content changes in low-perm. layer. Enhances resistance to infiltration through cover and contact of water with wastes

Primary barrier to infiltration of water through cover and radon flux to surface

Provides stable base for placement and compaction of low-perm. layer. May be unnecessary if wastes have been compacted or stabilized

Figure 1. Conceptual Design for Multi-Layer Waste Cover System with Riprap for Protection of Low-Permeability or Radon Barrier Layer



COMPOSITION

PURPOSE

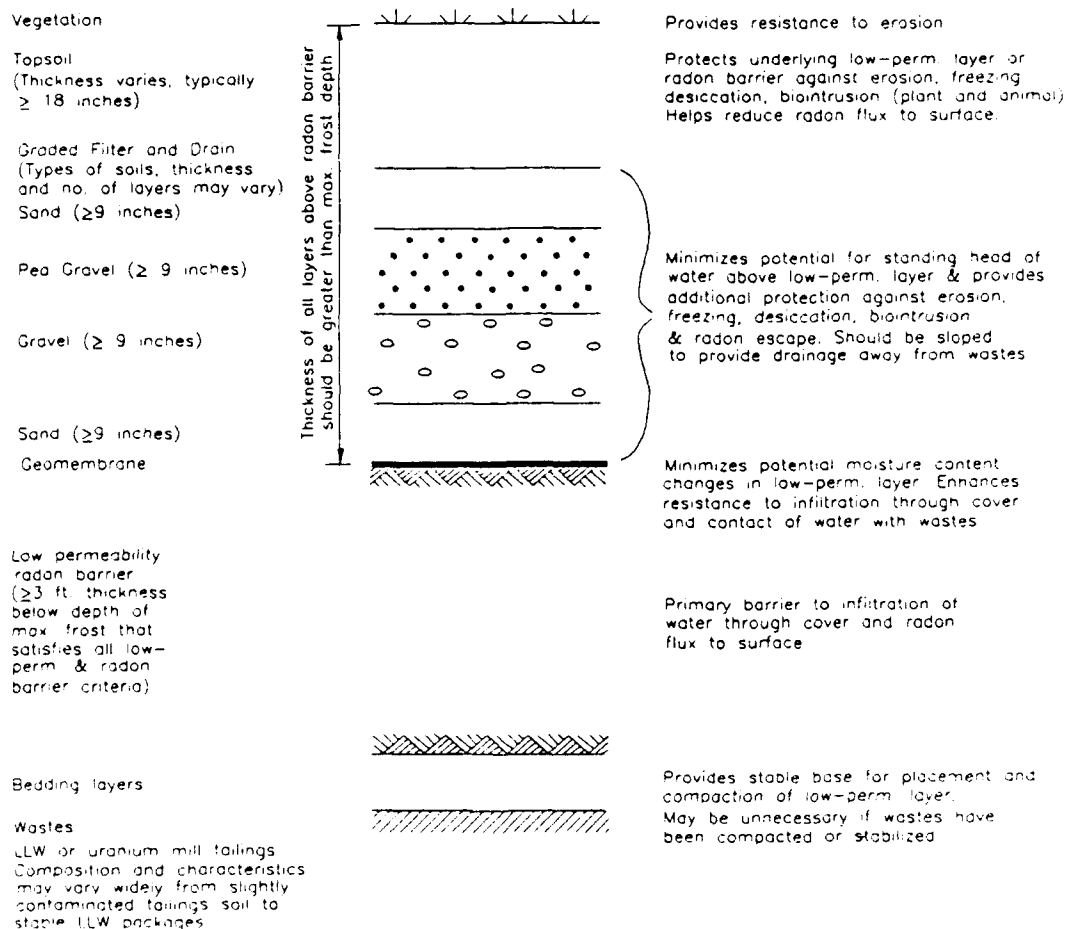


Figure 2. Conceptual Design for Multi-Layer Waste Cover System with Topsoil and Vegetation for Protection of Low Permeability or Radon Barrier Layer

performance and the test program that will allow reliable, efficient determination of these characteristics and properties. Cost and scheduling, considered alone, would favor use of a few quick, inexpensive, small scale index-type tests such as Atterberg limits, gradation, and moisture density determinations. Reliability and accuracy considered alone would favor use of more frequent, elaborate and larger scale tests. The obvious compromise is to use a sufficient number of large-scale, reliable tests, complemented by a larger number of small scale index tests. The index tests results must be capable of being correlated with the large-scale test results, and the correlations must be reliably established prior to construction, to develop an effective and efficient QA/QC test program that can be implemented to ensure satisfactory cover performance. In this regard, the soil characteristics and properties considered most important for waste covers are:

- Hydraulic conductivity or coefficient of permeability of low-permeability and filter and drainage layers
- Moisture-density relationships and correlations with hydraulic conductivity
- Soil gradation for classification, correlations, and filter requirements
- Atterberg limits for classification, correlations, and filter requirements
- Clay mineralogy (amount and type)
- Consolidation and swell characteristics
- Shear strengths

Other characteristics that are of concern for some soils or at some sites include erodibility and dispersiveness, radon flux, organic content, and gradation and durability of riprap or stone. Most of the soil properties and characteristics of interest are determined using standardized, non-controversial tests that are well understood and commonly used. However, the hydraulic conductivity of a waste cover is a critical measure of its expected performance, and its measurement is the subject of conflicting opinions and practices. Therefore, the following comments and recommendations are offered concerning hydraulic conductivity tests.

Hydraulic Conductivity (k)

Laboratory tests listed in Table 5 can yield accurate reliable values of hydraulic conductivity of laboratory scale specimens. The procedures, applications, potential problems, advantages, and disadvantages of each type of laboratory test and apparatus are generally well understood by the specialists that perform and evaluate these tests. Both the rigid wall and flexible wall laboratory permeameters have appropriate uses in waste cover design and construction. The rigid wall permeameter using the compaction mold is most practical for determining hydraulic conductivity of specimens compacted into the mold for design, to develop correlations between laboratory hydraulic conductivity and moisture-density, for construction QA/QC, and to characterize borrow materials. The flexible wall permeameter is most useful for QA/QC tests of hydraulic conductivity of undisturbed specimens from the completed cover or test section. Laboratory tests alone are not recommended for assurance of satisfactory waste cover performance. Laboratory tests do not include the effects of large-scale defects or macrofeatures and therefore tend to yield values of k that are unconservative, i.e. lower than actual



Table 5
LABORATORY HYDRAULIC CONDUCTIVITY TESTING REQUIREMENTS

Apparatus	Test Requirements and Procedures
Flexible wall Permeameter: Consolidometer type rigid wall	<ul style="list-style-type: none"> • Use permeant that approximates composition of field permeant. • Test specimen as large as possible • Test using stresses appropriate to field condition. • May be appropriate to test at several confining pressures. • General guidelines for testing using all flexible wall permeameters: <ol style="list-style-type: none"> (1) Backpressure to assure complete saturation. (2) Limit gradients to assure laminar flow. (3) Use guidance provided by ASTM draft std. (4) Prevent entry of air into specimen by separating air/permeant interface from specimen sufficiently or by using a membrane interface in permeant inlet reservoir. (5) Correct for temperature (6) For tests longer than 1 wk., take measures to prevent growth of microbes (7) Test until inflow rates and outflow rates are constant and equal; check for equilibrium no volume change. (8) Make plot of k vs. time - to note any increasing or decreasing trends.
Rigid wall Permeameter	<ul style="list-style-type: none"> • Use permeant that approximates composition of field permeant. • Test specimen as large as possible • If possible with apparatus used, control stresses on specimen to approximate field conditions. May be appropriate to test at several confining pressures. • Use divided outlet to check for sidewall effects. • Do not use with field compacted specimens due to difficulty of getting good fit. • Control gradients to assure laminar flow • Test until inflow rates and outflow rates are constant and equal. • Prevent entry of air into specimen by separating air/permeant interface from specimen sufficiently, or by using a membrane interface.
Recommendations for all k tests	<ul style="list-style-type: none"> • Insist on equal rates of inflow and outflow. • Insist on steady K with time. • Avoid excessive gradients. • Avoid excessive confining stresses • Need to saturate soil fully (or simulate field condition). • Use tap water or special permeant (std. solu.)
Recommendations for k Tests with Special Permeants	<ul style="list-style-type: none"> • Equal inflow and outflow. • Steady hydraulic conductivity. • At least 2 pore volumes of flow. • Influent/Effluent equilibrium <ul style="list-style-type: none"> - pH similar - full breakthrough of key ions • Check compatibility of membranes before doing flexible wall tests.

field values. Therefore, field methods that test larger volumes of soil and that are more likely to assess the effects of large scale defects are recommended to complement laboratory testing. Field tests on test fills allow correlations to be developed with laboratory tests for design and QA/QC. Large scale field tests such as the sealed double-ring infiltrometer or the underdrain pan lysimeter (Table 6) offer advantages for reliable measurement of hydraulic conductivity of a cover. Disadvantages include the time and costs required to perform these tests, and the potential disruptions and delays to the project. These tests are primarily recommended for performance assurance on test fills to avoid delays to the full scale project and to avoid damage to the integrity of the cover that can occur from these tests. Other field tests such as borehole falling or constant head tests summarized in Table 6 may also be effectively used to bridge the gap between laboratory scale tests and large scale field tests.

Waste Cover Construction Considerations

The approach used in developing these cover construction recommendations was to provide specific guidance that should ensure achievement of properties of the constructed cover that are considered essential to satisfactory long-term performance. It is recognized that site specific factors or design objectives may favor modification of some of these recommendations. If test results and analyses demonstrate that satisfactory performance can be ensured, alternative criteria may be appropriate.

These recommendations emphasize a combination of performance criteria or specifications, and certain minimum method and material specifications. This approach is believed to be more effective in producing satisfactory projects completed at reasonable costs, because the contractor is given the freedom to choose and control proper use of equipment, personnel, and material to achieve the required end result. To be successful this approach to design and construction requires a strong and explicit program for quality control and assurance (QA/QC). The QA/QC program must identify responsibilities of the various parties involved in the project, the parameters to be tested, test methods and frequencies, allowable values or tolerances of measured parameters important to performance, and the corrective actions to be taken when deficiencies are measured or observed. The need for trained, experienced personnel to execute the design cannot be over-emphasized.

The total thickness of the low-permeability cover layer should be sufficient to limit radon release and surface dose rates to acceptable levels and minimize infiltration. This layer should be at least 3-ft thick. Relatively thick clay layers built up with several thin lifts offer several advantages over thin layers or geomembranes used alone. For example, small defects are unlikely to be continuous throughout the full thickness of the cover layer. Thicker layers result in longer times for complete saturation to occur throughout the cover thickness and longer travel times and paths for infiltration through the cover. Lower values of hydraulic conductivity may also be obtained as a result of closing of macrofeatures of the soil mass caused by higher confining stresses from the weight of overburden. In a study of clay liners from test pads in Texas, Daniel found that hydraulic conductivity, k , did decrease as liner thickness increased (Daniel, 1990). The decrease in k was largest as liner thickness increased from 1.0 to 2.0 ft. The decrease in k as liner thickness increased from 2.0 to 4.0 ft was



Table 6
ADVANTAGES AND DISADVANTAGES OF
VARIOUS IN SITU HYDRAULIC CONDUCTIVITY TESTS¹

Type of test (1)	Device (2)	Advantages (3)	Disadvantages (4)
Borehole	Boutwell permeameter	Low equipment cost (<\$200 per unit). Easy to install. Hydraulic conductivity is measured in vertical and horizontal direction. Can measure low hydraulic conductivity (down to about 10^{-9} cm/s). Can be used at great depths on slopes.	Volume of soil tested is small. Unsaturated nature of soil not properly taken into account. Testing times are somewhat long (typically several days to several weeks for hydraulic conductivities $<10^{-7}$ cm/s).
	Constant head permeameter	Low equipment cost (<\$1000 per unit). Easy to install. Unsaturated nature of soil taken into account relatively rigorously. Relatively short testing times (a few hours to several days). The hydraulic conductivity that is measured is primarily the horizontal value (which is an advantage if this is the desired value). Can be used at great depths.	Volume of soil tested is small. The hydraulic conductivity that is measured is primarily the horizontal value (in some applications, the value in the vertical direction is desired). The device is not well suited to measuring very low hydraulic conductivities (less than 10^{-7} cm/s).
Porous probe	BAT permeameter	Easy to install. Short testing times (usually a few minutes to a few hours). Probe can also be used to measure pore-water pressures. Can measure low hydraulic conductivity (down to about 10^{-10} cm/s). The hydraulic conductivity that is measured is primarily the horizontal value (which is an advantage if this is the desired value). Can be used at large depths.	High equipment cost (>\$6000). Volume of soil tested is very small. Soil smeared across probe during installation may lead to underestimation of hydraulic conductivity. The hydraulic conductivity that is measured is primarily the horizontal value (in some applications the value in the vertical direction is desired). The unsaturated nature of the soil is not properly taken into account.
Infiltrometer	Open, single-ring infiltrometer	Low cost (<\$1000). Easy to install. Very large infiltrometer can be used to test a large volume of soil. Hydraulic conductivity in the vertical direction is determined.	Low hydraulic conductivity ($<10^{-7}$ cm/s) is difficult to measure accurately. Must eliminate, or make a correction for, evaporation. May need to correct for lateral spreading of water beneath infiltrometer. Testing times are relatively long (usually several weeks to several months for hydraulic conductivities $<10^{-7}$ cm/s). Must estimate wetting-front suction head. Cannot be used on steep slopes unless a flat bench is cut.
	Open, double-ring infiltrometer	Low equipment cost (<\$1000). Hydraulic conductivity in the vertical direction is determined. Minimal lateral spreading of water that infiltrates from inner ring.	Low hydraulic conductivity (10^{-7} cm/s) is difficult to measure accurately. Must eliminate or make a correction for evaporation. Testing times are somewhat long (usually several days to several months for hydraulic conductivities $<10^{-7}$ cm/s). Must estimate wetting-front suction head. Cannot be used on steep slopes unless a flat bench is cut.
	Closed, single-ring infiltrometer	Low equipment cost (<\$1000). Hydraulic conductivity in the vertical direction is measured. Can measure low hydraulic conductivity (down to 10^{-8} - 10^{-9} cm/s).	Volume of soil tested is somewhat small because diameter of ring is <1 m. Need to correct for lateral spreading of water if wetting front penetrates below the base of the ring. Testing times are long (usually several weeks to several months).

Table 6 (CONCLUDED)
ADVANTAGES AND DISADVANTAGES OF
VARIOUS IN SITU HYDRAULIC CONDUCTIVITY TESTS¹

Type of test (1)	Device (2)	Advantages (3)	Disadvantages (4)
	Sealed, double-ring infiltrometer	Moderate equipment cost (<\$2500) Hydraulic conductivity in the vertical direction is determined. Can measure low hydraulic conductivity (down to about 10^{-8} cm/s). Minimal lateral spreading of water that infiltrates from inner ring. Relatively large volume of soil is permeated.	Must estimate wetting-front suction head. Very difficult to use on steeply sloping ground. Testing times are relatively long (usually several weeks to several months). Must estimate wetting-front suction head. Cannot be used on slopes unless a flat bench is cut.
	Air-entry permeameter	Modest equipment cost (<\$3000) Relatively short testing times (a few hours to a few days) Hydraulic conductivity in the vertical direction is measured. Can measure low hydraulic conductivity (down to 10^{-8} - 10^{-9} cm/s) Wetting-front suction head is estimated in second stage of test.	A relatively small volume of soil is permeated because the wetting front usually does not penetrate more than a few centimeters into compacted clay. Cannot be used on slopes unless flat bench is cut. Several important assumptions are required.
Underdrain	Lysimeter pan	Low cost. The hydraulic conductivity in the vertical direction is measured. Large volumes of soil can be tested. Few experimental ambiguities. No disturbance of soil.	Must install underdrain before the liner is constructed. Relatively long testing times (usually several weeks to several months for hydraulic conductivities less than 10^{-7} cm/s). Must collect and measure seepage from underdrain, which usually necessitates a sump and a pump.

¹ Ref. Daniel, 1989

approximately one-half an order of magnitude, but the decrease in k was one and one-half orders of magnitude as the liner thickness increased from 1.0 to 2.0 ft. Potential frost damage is less likely to fully penetrate and impair the performance of thick clay layers.

A drainage layer should be provided at sites where needed to remove any water that infiltrates before it reaches the disposed wastes. A filter layer may be required to prevent adjacent fine-grained soil particles from migrating into and clogging a relatively coarse-grained drainage blanket. Filter and drainage systems should be capable of providing long-term satisfactory performance in minimizing the contact of water with wastes, but to perform as intended, the filter and drainage system should meet certain fundamental requirements described elsewhere (Winterkorn and Fang, 1975; Denson et al., 1987). These requirements cover proper selection, gradation, placement, and compaction necessary to achieve design drainage rates and volumes, and prevent internal erosion and piping.

Testing and Acceptance Criteria

Low-Permeability Soil Layers. Historically, fill placement specifications have been developed based on criteria for strength and settlement. Low permeability has, in many cases, been an important but secondary consideration. In most cases it was assumed that achievement of a specified minimum density would guarantee achievement of required low-permeability values. However, reexamination of previous studies (Mitchell et al., 1965) and recent research (Daniel and Benson, 1990; Benson and Daniel, 1990) has shown that low permeability cannot be assured through specification of a given minimum density. In fact, in some cases, soil covers compacted according to traditionally accepted specifications, with good quality control in the field, failed to satisfy the permeability criterion (Daniel, 1987). Laboratory compaction and permeability tests showed further evidence that the density - moisture content - permeability relationships were not adequately explained by nor was adequate performance ensured by traditional approaches.

An innovative approach for developing practical criteria for insuring satisfactory performance of low-permeability soil layers proposed by Daniel and Benson (1990) is illustrated in the plots shown in Figure 3.

The important conclusion from this study shows that acceptable hydraulic conductivity values are more readily achieved with soils compacted on the wet side of optimum and with heavy compactive effort. Soils compacted wet of optimum moisture content can satisfy the low hydraulic conductivity criterion for a wider range of dry densities than soils compacted on the dry side of optimum. Soils placed with heavy compactive effort met the required low hydraulic conductivity criterion for a wider range of moisture contents (including moisture contents on the dry side of optimum) than soils placed with lower compactive effort.

Acceptance of compaction of the low-permeability soil fill for use in covers should be based on achievement of a specified minimum dry density and at the specified range of moisture content during compaction for each lift placed. The specified density and moisture contents should be correlated with and based on achievement of required hydraulic conductivity, shear strength, and other important performance characteristics that are not as readily



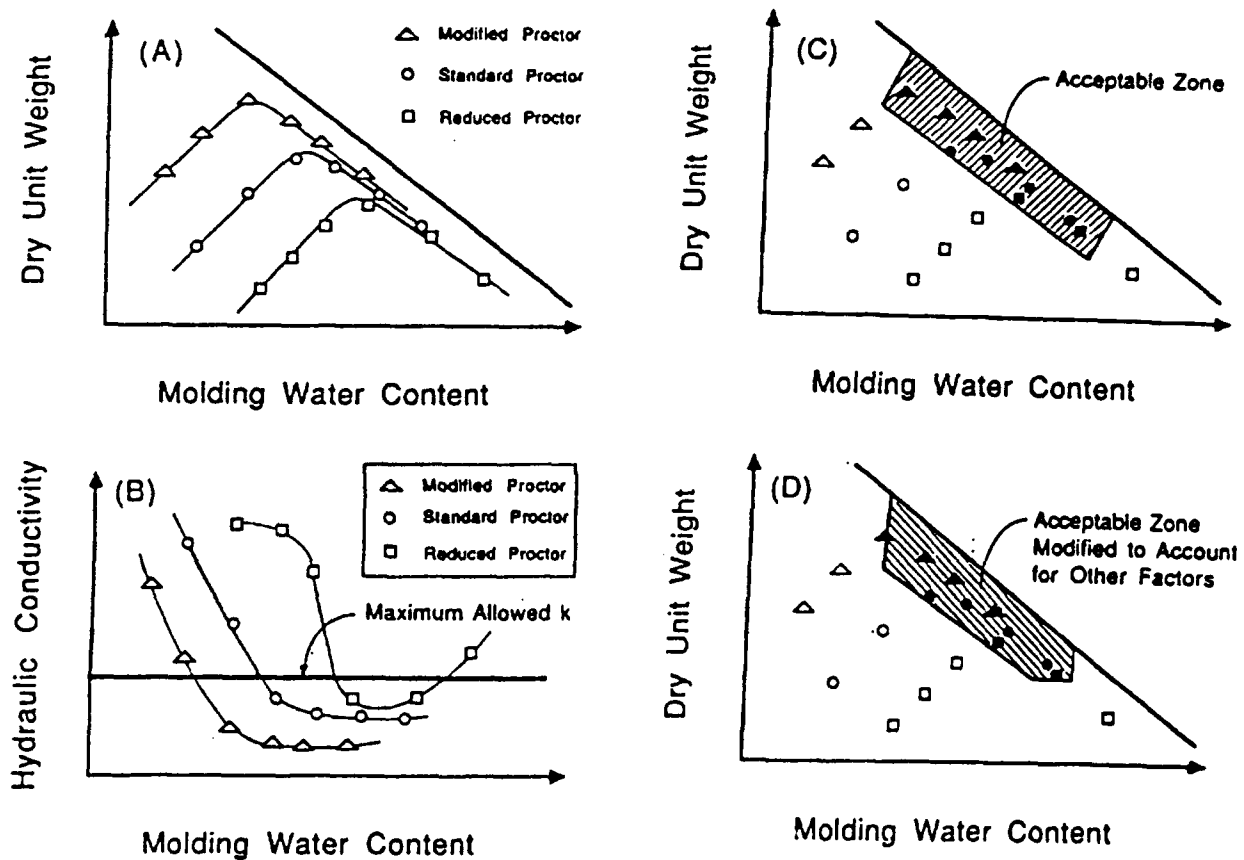


Figure 3. Illustration of Daniel and Benson Method for Developing Fill Compaction Control Specifications Based on Design Criteria for Hydraulic Conductivity, Shear Strengths and Other Parameters (Daniel and Benson, 1990)

determined as the more common moisture and density values. Specific tests to ensure achievement of these properties should be periodically performed, but such tests may be performed at longer intervals. A recommended test plan is offered in Table 7. For testing of low-permeability soil layers, approximately half of all test locations should be predetermined randomly and the remainder should be at suspected problem areas. Tests should be performed during construction at the completion of compaction of each lift or section of a lift. Again, modifications or additions to the test frequencies may be required for specific projects and these recommendations are offered as a reasonable basis from which to develop site specific programs.

Filter and Drainage Layers. Specific guidance on field testing for filter and drainage layers for uranium mill tailings and low-level radioactive waste disposal covers is offered in Table 8. In cohesionless soils, density tests cannot be properly conducted at the ground surface, due to the lack of confinement. Therefore, tests for filter and drainage layer acceptance should be performed one lift below the surface. Approximately half of all tests should be run at locations chosen randomly prior to construction and the remainder should be run at suspected problem areas. Tests should be performed concurrent with construction. It is recognized that modifications or additions to the testing plan may be warranted for some sites, based on tests and analyses performed during design and construction.

Conditioning or Processing of Low-Permeability Soils

Low-permeability soils usually require processing before use as a cover layer to adjust moisture content, pulverize clods, and remove oversize and objectionable materials to achieve required satisfactory long-term performance. Maximum size of clods should be less than half the compacted lift thickness.

Oversize material in low-permeability soils such as rock fragments larger than 1 in. should be removed by screening, crushing or special rakes. Screening will also remove remnants of limbs, roots, stumps, and other objectionable oversize debris materials that may have been inadvertently excavated with the low-permeability soils. Some hand work may be required as a final step to ensure that all objectionable materials have been removed.

Placement and Compaction of Low-Permeability Soils

Recommendations for placement and compaction of low-permeability soils for waste covers are summarized in Table 9. During placement of the low-permeability cover, final adjustment of moisture content may be required and can be accomplished by disking or tilling. The timing of placement and compaction should allow complete hydration of moisture added to the soil, so that water completely penetrates the clods. This condition can be easily verified by breaking up clods by hand to check appearance and by testing moisture contents for uniformity throughout the soil mass. Soils that are too wet may be disked or tilled to allow evaporation and reduction of soil moisture content prior to compaction but it is difficult to dry out soils more than a few percent below existing water contents.

The surface of individual lifts and the final cover should be protected from desiccation to prevent cracking and from freezing to prevent heave damage

Table 7. Recommended Tests and Test Frequencies in Construction of Low-Permeability Cover Layers for Uranium Mill Tailings and Low-Level Radioactive Waste Projects

Test or Observation	Recommended Frequency ¹	
	Unrestricted Areas	Restricted Areas
Loose Lift Thickness*	5/acre/lift	At 2000 ft ² intervals and at critical locations
Lift Bond*	2/acre/lift	At 2000 ft ² intervals and at critical locations
No. of Passes** or Coverages	2/acre/lift	Each lift
Field Density & Moisture Content and 2 pt Lab Compaction Test ²	At 10,000 ft ² (app. 175 yd ³) interval	At 2000 ft ² (app. 35 yd ³) or at least 1 per lift
5 pt Lab Compaction for Moisture-Density Curve ²	At 2000 yd ³ intervals and when material changes	At 2000 yd ³ intervals and when material changes
Grain Size (Sieve and Hydrometer Analysis)***	At 1000 yd ³ intervals and when material changes	At 1000 yd ³ intervals and when material changes
Atterberg Limits	At 1000 yd ³ intervals and when material changes	At 1000 yd ³ intervals and when material changes
Lab Hydraulic Conductivity of Remolded Compacted Specimens	When material changes and when field hyd. cond. tests are run	When material changes and when field hyd. cond. tests are run
Field Hydraulic Conductivity	On test fills	On test fills

¹ Test frequency and test methods may require modification to accommodate specific site conditions, design requirements, and regulations.

² Tests should be performed at locations chosen randomly prior to construction for approximately half of the total and at suspected problem areas for the remainder of the tests.

* By observation, using shovel to check for thickness of loose lifts and visual laminations or weak zones in compacted lifts.

** A pass is defined as a complete application over the entire surface of the lift, i.e. by rubber tires, roller, drum, or treads of a crawler tractor. For a sheepfoot roller, one pass consists of one movement of the sheepfoot roller drum over the area being compacted.

*** Only +No. 4 and -No. 200 fractions required for CL and CH.



Table 8. Recommended Tests and Test Frequencies in Construction of Filter and Drainage Cover Layers for Uranium Mill Tailings and Low-Level Radioactive Waste Projects

Test or Observation	Recommended Frequency ¹	
	Unrestricted Areas	Restricted Areas
Loose Lift Thickness*	5/acre/lift	At 2000 ft ² intervals and at critical locations and at least once each lift
No. of Passes**	Each lift	Each lift
Field Density and Moisture Content and 2 pt Lab Comp. Test ²	1 per 1000 yd ³ and when material changes	1 per 500 yd ³ and when material changes
Maximum Density	Same frequency as field density, i.e. 1/1000 yd ³ and when material changes	1/500 yd ³ and when material changes
Minimum Density	Same frequency as field density, i.e. 1/1000 yd ³ and when material changes	1/500 yd ³ and when material changes
Grain Size (Sieve Analysis)	1/1000 yd ³ intervals and when material changes	1/1000 yd ³ intervals and when material changes
Laboratory Hydraulic Conductivity	When material changes	When material changes

¹ Test frequency and test methods may require modification to accommodate specific site conditions, design requirements, and regulations.

² Tests should be performed at locations chosen randomly prior to construction for approximately half of the total and at suspected problem areas for the remainder of the tests. All tests should be performed one lift below the surface. Tests should be performed concurrent with construction of each lift.

* Visual observation, using shovel to check thickness of lifts.

** A pass is defined as a complete application over the entire surface of the lift, i.e. by rubber tires, roller, drum, or treads of a crawler tractor. For a sheepfoot roller, one pass consists of one movement of the sheepfoot roller drum over the area being compacted.

Table 9. Recommended Placement and Compaction Specifications for
Low Permeability Cover Soils for Uranium Mill Tailings and
Low-Level Radioactive Waste Projects

Recommended Specification Item	Unconfined or Open Areas	Confined or Restricted Areas
Loose Lift Thickness	≤ 9 in.	4 in.
Compacted Lift Thickness	6 in.	2 to 3 in.
Min. Dry Density*	Greater of 92% of max. dry density as det. by Mod. Proctor (ASTM D 1557) or the min. reqd. to achieve design objectives, e.g. shear strengths, compressibility, hydraulic conductivity, and resistance to cracking and shrinkage.	Greater of 92% of max. dry density as det. by Mod. Proctor (ASTM D 1557) or the min. reqd. to achieve design objectives, e.g. shear strengths, compressibility, hydraulic conductivity, and resistance to cracking and shrinkage.
Placement Moisture Content*	Select acceptable range to achieve design objectives such as shear strengths, compressibility, hydraulic conductivity, and resistance to cracking and shrinkage. Typical range is optimum to 3% above optimum, det. by ASTM D 1557 (Modified Proctor)	Select acceptable range to achieve design objectives such as shear strengths, compressibility, hydraulic conductivity, and resistance to cracking and shrinkage. Typical range is optimum to 3% above optimum, det. by ASTM D 1557 (Modified Proctor)
Scarification**	Each lift to 1 in. depth	Each lift to 1 in. depth
Typical No. of Passes or Coverages Required**	Rubber tired rollers - 2 to 4 Sheepsfoot rollers - 4 to 8	Portable vibratory plate tampers and portable roller compactors weighing at least 900 lbs.
Suitable Compaction Equipment**	Heavy pad foot, sheepsfoot or rubber-tired rollers.	Overlap areas compacted by heavy equipment
Direction of Coverage of Compaction Equipment**	Alternate direction of each pass perpendicular to direction of previous pass.	Same, to extent possible.
Compaction Equipment Operating Speed***	Typically 1.5 to 5 mph	

- * These recommendations differ from guidance given in NUREG/CR-5041, which was developed for LLW covers above relatively rigid engineered facilities and was more prescriptive. The wide variability of UMTRA and LLW site conditions that may be encountered requires more flexible, general guidance.
- ** Corps of Engineers Guide Specification CW-02212 provides additional guidance on selection and operation of compaction equipment.
- *** Operating speed of compaction equipment directly influences compactive energy. Low operating speeds should be used for soils that are difficult to compact, for high density requirements, and when thick lifts are placed.



and to prevent adverse impacts on hydraulic conductivity. Frozen soils should not be placed in the cover nor should soils be compacted when the underlying surface is frozen, muddy, or cracked. Erosion damage should be prevented or the damaged area repaired. Protection from erosion damage during inclement weather may be provided by sloping and proper drainage, rolling with a smooth drum roller to seal the surface, and for relatively small areas by covering with plastic sheeting or tarpaulins. Protective soil layers, if used, should be removed and the underlying lift tested for compliance with moisture and density specifications before resumption of construction activities. It is sometimes more cost-effective to simply remove lifts or portions of lifts damaged by freezing, erosion, or desiccation than to prevent the damage.

Unrestricted or Open Areas. In unrestricted or open areas, where high-volume compaction equipment can be used, the low-permeability soils should be placed in loose lift thicknesses of not more than 9 in., so that compacted lifts are not more than approximately 6 in. thick. Thin lifts are necessary to ensure good bonding between lifts.

The upper surface of each lift should be scarified to about 1 in. by disking to promote bonding with the next lift and to prevent formation of preferential flow paths or weak interfaces. The first lift, or bedding layer must be carefully placed and compacted to prevent damage to the underlying material such as geomembranes, geotextiles, or drainage layers. It may be impractical to fully compact the first lift to specifications, especially if a thick lift is used to avoid damage to underlying materials. If this is the case, the first lift should not be included in the measurement of minimum total cover thickness achieved. The direction of operation of compaction equipment should be alternated after each complete coverage or pass to be perpendicular to the pass just completed. Perpendicular alternating travel routes minimize the potential risks that directional anomalies will develop or that turn around or edge areas will be inadequately compacted. A smooth drum or rubber-tired roller should be used to finish the upper surface of the final lift to minimize the development of preferential flow paths and potential gullying. Smooth drum and rubber-tired rollers may also be effectively used to seal surfaces to minimize erosion, wetting or drying during periods of inactivity.

Restricted or Confined Areas. In confined or restricted areas, the soil should be placed in lifts not more than 4-in. thick and compacted with portable equipment such as rammer compactors to achieve minimum required density within specified ranges of moisture content. These specified density and moisture values should be the same as used for unrestricted areas. All other guidance given for open areas applies to restricted areas. Care must be exercised near engineered features such as geomembranes, geotextiles, disposal structures, monitoring wells, instruments, and adjacent soil layers to prevent damage from equipment. It is often necessary to experiment and modify field procedures for lift thickness and compaction effort in confined areas, to achieve desired results. Close control and testing is recommended in these areas especially during initial stages of construction.

Slopes. Placement and compaction of soils on slopes require special consideration. The energy component imparted by compaction equipment normal to the slope surface is proportionally less than for horizontal lifts. In addition the soil may "walk" or flow downslope, resulting in thinner lifts

near the crest and thicker lifts near the toe. Traction and equipment stability are also impaired when working on slopes. For slopes flatter than 3H:1V, some equipment can travel, unassisted, parallel, up and down the slope and satisfactory compaction may be achievable, but should be verified by testing. For slopes steeper than 3H:1V, unassisted travel is difficult, and for slopes steeper than 2.5H:1V, is usually not practical.

Conditioning or Processing of Filter and Drainage Soils

Processing of filter and drainage materials prior to use in covers is often necessary to achieve required gradation and to remove undesirable materials. However, processing of coarse-grained soils is generally much simpler than for fine-grained cover soils. The soil may require coarse screening to remove oversize material, roots, limbs, or other debris. In some cases excessive fines may be removed to increase drainage rates and prevent clogging. Control of soil moisture content is not as critical as for fine-grained soils and may be achieved more readily. Screening operations are more important in cases where relatively thin graded filters are required to achieve satisfactory drainage rates and protect adjacent soils from piping and internal erosion. Filter materials are often stockpiled when it is necessary to obtain such materials from commercial sources or to manufacture them on the site. Care should be taken in stockpiling and placing filter materials to avoid segregation, contamination, and particle breakage.

Placement and Compaction of Filter and Drainage Layers. Recommended procedures and specifications are given in Table 10 and are discussed below.

Unrestricted Areas. In unrestricted or open areas, where normal, high volume compaction equipment can operate, the filter and drainage layer materials should be placed in loose lifts not more than 12 in. thick. Each lift should be compacted using equipment and methods that have been shown to be effective for the site or similar sites and soil conditions. For example heavy vibratory smooth steel drum rollers or rubber-tired rollers provide effective compaction of coarse-grained materials. Heavy crawler tractors can be effectively used. Care must be exercised to ensure that grains are not crushed and that segregation does not occur during compaction.

Restricted Areas. In restricted or confined areas, portable equipment is required to avoid damage to structural features such as monitoring wells, collector sumps, or intermixing of different soils. This equipment typically cannot provide compactive efforts as high as is possible with heavy smooth steel wheel rollers or rubber tired rollers. Therefore, relatively thin loose lifts not more than 4 to 6 in. thick should be placed and compacted using portable equipment that has been shown to be capable of producing satisfactory results, such as vibratory plate or vibratory drum compactors. The relative density and moisture content requirements should be the same as for unrestricted areas. If performance criteria can be achieved at lower density or at moisture conditions other than specified values, consideration may be given to modifying the recommendations shown in Table 13.

Slopes. The same concerns for placement and compaction of low-permeability soils on slopes apply to placement and compaction of drainage layers on slopes. The need to intensify quality control and inspection of fill placed on slopes is equally important and applicable to drainage blanket

Table 10. Recommended Placement and Compaction Specifications for Pervious
Soils Used for Filter and Drainage Cover Layers for Uranium
Mill Tailings and Low Level Radioactive Waste Projects

<u>Recommended Specification</u>	<u>Unconfined or Open Areas</u>	<u>Confined or Restricted Areas</u>
Loose Lift Thickness	≤ 12 in.	4 to 6 in.
Minimum Dry Density, γ_d	75% D_R^* or 92% of maximum dry density as determined by ASTM D 4253 and D 4254 or D 1557, respectively	75% D_R^* or 92% of maximum dry density as determined by ASTM D 4253 and D 4254 or D 1557, respectively
Placement Moisture Content, w%	≤ 1% or saturated	≤ 1% or saturated
Suitable Compaction Equipment	Vibratory smooth steel drum roller compactors, rubber tired compactors, crawler tractors.	Portable vibratory plate tamper and portable vibratory roller compactors weighing at least 900 lbs. Overlap areas compacted by heavy equipment.
Compaction Equipment Operating Speed**	Typically 1.5 to 5 mph	

* D_R = Maximum Relative Density per ASTM D 4253 and D 4254

The test method used for establishing and controlling minimum dry density requirements should be selected based on soil gradation and plasticity characteristics.

Segregation of particle sizes or crushing of soil grains during handling, placement, and compaction must be avoided. Excessive compactive efforts and unnecessary rehandling or movement should therefore be avoided.

** Operating speed of compaction equipment directly influences compactive energy. Low operating speeds should be used for high density requirements and when thick lifts are placed.



construction.

Remediation of Cover Deficiencies. On almost any project, quality control test results and inspections will indicate occasional failure to satisfy specifications for moisture or density or other required characteristics. Even with very careful construction methods and vigilant inspection, some failures to meet specifications may be indicated by test values. The failures may be more frequent at the beginning of a project, after temporary shutdowns during inclement weather or after winter shutdowns. Since these occurrences can be expected, a rational plan for dealing with these exigencies should be developed and made part of the contract documents, so that small deficiencies can be corrected without delays and resultant cost increases. It is desirable to try to determine the cause of unsatisfactory conditions, so that the condition can be corrected or avoided in subsequent work.

In any case where a deficiency is observed and corrective action is required, the deficient zone should be determined through review of test results and additional testing, as required. Usually, only the deficient areas within a lift should be reworked but these must be reworked to the full depth of the lift. There is no justification for removing an entire lift or an entire cover if only a small, well-defined deficient zone can be reworked and brought within specifications. Areas that have been reworked should, of course, be re-tested to ensure compliance with specifications.

Test Fills and Test Pads. Test fills and test pads can be quite useful for "debugging" a design and developing construction specifications that will promote efficient use of materials, equipment, and labor to construct a cover that will give long-term satisfactory performance. Test fills are especially useful for unusual soils or marginally acceptable soils or when method and materials specifications are used in the construction contract. To obtain the advantages of a test fill program, it must be carefully planned and executed so the results can be used to improve the design.

To be able to evaluate the test fill results and compare these results to the full size cover, it is essential that the proposed materials, processing, placement and compaction methods, and other major features called for in the design be exactly duplicated in the test fill. Climatic conditions can affect results, especially moisture contents, so seasonal differences should be avoided in so far as possible between construction of the test fill and full size cover. On large projects, it may be reasonable to examine a range of materials, methods, and equipment, but the control test fill case should duplicate the design for the full-size cover for meaningful evaluation. Test fills should be long enough to allow compaction equipment to reach normal operating speed over the area to be tested and wide enough for at least 3 contiguous passes of compaction equipment. Lift and total cover thickness should usually be as specified for the full size cover. If potential problems are anticipated for cover construction on slopes or confined areas, these areas should receive attention during the test fill program. Similarly, if the investigation of borrow sources indicates wide variability in material properties, it may be necessary to construct portions of the test fill using the range of materials anticipated to be excavated and to determine the performance characteristics within this range. Test fills can also be quite useful for developing correlations between field and laboratory tests of the

same property, e.g., hydraulic conductivity, or correlations between index properties that may be quickly determined and the important performance characteristics that may require longer periods of time to reliably determine. Test fills may also be useful for developing repair methods and testing their effectiveness. In general, the same criteria and test methods should be used to evaluate test fills as will be used on the full-scale cover. However, the control tests should be run more frequently to obtain the most benefit from the program. In addition, longer term or large scale in situ tests such as pan lysimeter or double ring infiltrometer tests can be run to verify the results of laboratory hydraulic conductivity tests and to develop correlations for use on the full size cover.

Construction Records. Complete records of cover construction should be developed, organized, and maintained. Such records would be invaluable if performance problems develop and would be extremely useful for design and construction of subsequent waste cover projects from the perspective of lessons learned and problems faced and solved.

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Design Optimization of In-Situ Volatilization Systems

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ABSTRACT

The Twin Cities Army Ammunition Plant (TCAAP) located in New Brighton, Minnesota has experienced, due to past disposal practices, soil contamination by volatile organic compounds (VOC) at several isolated disposal sites. Although several VOC's have been identified, the principal pollutant is 1,1,2 trichloroethylene (TCE). Soil samples analyzed before remedial action commenced have shown VOC concentrations in excess of 5000 milligrams per kilogram (mg/kg). During the remedial investigation it was determined to conduct an interim remedial measure, an in-situ volatilization (ISV) system. Since implementation of the ISV system at TCAAP Site D in late January of 1986 in excess of 100,000 lb. of total VOC's (as measured in the air flow from the system) have been removed from the soil. However, verification of the extent of soil cleanup and effectiveness of the present system design have been difficult to assess.

In order to better understand the ISV process and provide a tool for the design optimization and evaluate the effectiveness of these systems, a numerical simulator was developed. This multi-

dimensional, multi-phase transport simulator incorporates mass-partitioning between the soil, water, vapor and oil phases. The results of the numerical simulations indicate that while VOC as an irreducible oil phase may be induced to volatilize fairly rapidly, VOC within the water phase may keep air phase concentrations detectable for long periods of time. In particular, air phase concentration rebounds related to blower shutdown and startup have been observed and related to the presence of VOC as an oil phase. The numerical model of TCAAP Site D has been able to reproduce the general features of that ISV system.

INTRODUCTION

When volatile organic chemicals are a contaminant of interest in an unsaturated soil system, in-situ volatilization may be the remediation methodology of choice. ISV remediation systems are comprised of extraction vents which draw VOC rich soil air to surface collection manifolds and thereby reduce the soil contamination. The great benefit of this remediation technique is that contaminated soils may be left in place during the cleanup process, thus creating a great cost savings. This project has developed a numerical scheme for determining the fate and transport of VOC in the unsaturated zone resulting from forced volatilization and gaseous advection-dispersion of organic vapor in a multi-partitioned three-dimensional environment. The numerical code is designed to be run on a IBM personal computer. Specifically the

code was developed to investigate ISV remediation strategies and predict the extent of ISV cleanup from information obtained at a limited number of data points, such as extraction vents. The three-dimensional model was used to replicate the operational data from an existing ISV remediation site at TCAAP. The results of that numerical exercise demonstrated the applicability of the code for making predictions of ISV performance and assisting in ISV remediation design. This new tool may be used by remediation designers to help plan cleanup strategies.

METHOD OF ANALYSIS

The transport code requires a companion simulator capable of predicting the velocities in the gas and/or water phases. The companion simulator used in the validation exercise of this report is the Eisenbeis et al. (1989) Colorado State University Gas Flow model (CSUGAS), a compressible gas flow code.

The transport model is capable of investigating the sensitivity of the ISV remediation method to the various physical processes and parameter values that determine its performance. Included among these processes and parameters are the isotherm adsorption model type, values of Henry's Law partitioning constant, soil temperature, VOC type, soil moisture content, values of intrinsic soil and environmental parameters, areal and vertical pressure vent spacing and patterns, and pressure vent collection and injection (air flooding) scenarios. Typically, multi-phase numerical flow simulators assume equilibrium conditions between the

phases. This assumption is not substantiated by field observations. Instead, field data suggests that temporal considerations play a large role in the inter-phase mass transfer process. This research has responded to these observations by using kinetic-driven inter-phase mass transfer partitioning functions which are also equilibrium sensitive. In addition, this research has focused on equations-of-state that are functions of pressure and not density. Other researchers (Sleep and Sykes, 1989, and Corapcioglu and Baehr 1987) have investigated density driven flow. While appropriate in unperturbed soil environments, the assumptions associated with density-driven flow are not suited to conditions under the influence of large externally imposed pressure gradients such as those typically associated with ISV systems. This study has focused on a single component oil which exists in irreducible saturation in an unsaturated soil environment.

MATHEMATICAL DESCRIPTION OF TRANSPORT

The analysis began by developing equations pertinent to the physics of mass transport within an unsaturated flow environment. Source-sink functions that describe the kinetic/thermodynamic mass transfer between phases were then incorporated into these equations. As the numerical model is designed for kinetic interactions, the mass transport is therefore phase specific. This development necessitates a mass transport equation for each phase. These equations are then rendered into finite difference form and solved numerically.

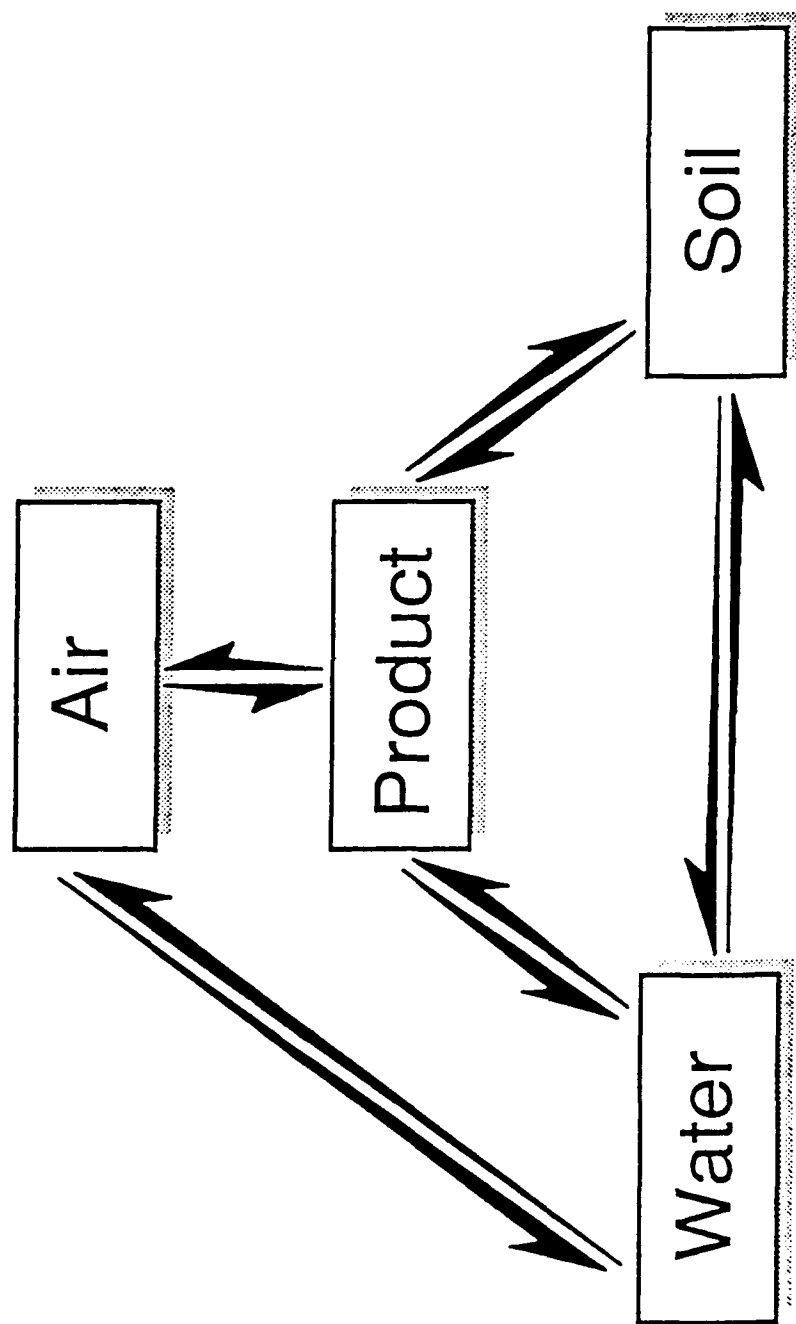


FIGURE 1. The Four Phase System
Arrows indicate the interphase mass transfer

The volatile hydrocarbon may reside within the water, vapor, soil and pure liquid phases. The hydrocarbon may also move between these phases. Figure 1 illustrates these phenomena. In order to account for this behavior interphase mass transfer functions were developed. Both the thermodynamic and kinetic aspects of interphase transfer of organic chemicals are considered in describing the mass partitioning process. The partitioning functions used in the present research assume mass transfer is an 1st order expression of the deviation from the equilibrium state (Castellan, 1971). This can be stated mathematically as

$$dc/dt = \lambda (C - C_{eq}) \quad 1$$

where: $C_{eq} = f(T)$ is a function of temperature only. Equation 1 is formulated to be sensitive to an equilibrium condition C_{eq} . When C is equal to C_{eq} the right hand side of Equation 1 is equal to zero and no mass transfer occurs. The equilibrium concentration C_{eq} is a function of temperature and determined from the thermodynamic definition of the phase-change process. The kinetic constant dimensionally has units of inverse time. Physically it incorporates effects of the phase velocity, system dimensions and mass transfer surface phenomena. The hydrocarbon interphase mass transfer coefficients include, vapor-liquid hydrocarbon partitioning (λ_{vo}), water-vapor partitioning (λ_{H}), soil-water partitioning (λ_{sw}), water-liquid hydrocarbon (λ_{D}) partitioning and soil-liquid hydrocarbon partitioning (λ_{so}). A value for C_{eq} can be thermodynamically determined for each of these

processes.

Equations were developed for three-dimensional advective-dispersive transport of a single component VOC in a variably saturated media. In that derivation it was assumed that the oil phase was in irreducible saturation and consequently immobile. For the vapor phase

$$\frac{\partial}{\partial x_i} (\phi S_V D_{Vij} \frac{\partial C_V}{\partial x_j}) + \phi S_V \lambda_{VO} (C_{ev} - C_V) + \phi S_V \lambda_H (HC_W - C_V)$$

$$+ q_V (C_V^* - C_V) - V_{Vi} \frac{\partial C_V}{\partial x_i} = \phi S_V \frac{\partial C_V}{\partial t}$$

2

water phase

$$\frac{\partial}{\partial x_i} (\phi S_W D_{Wij} \frac{\partial C_W}{\partial x_j}) + \phi S_V \lambda_H (C_V - HC_W) + \phi S_W \lambda_{SW} \rho_S (C_S - C_W K_{SW})$$

$$+ \phi S_W \lambda_D (C_{ew} - C_W) + q_W (C_W^* - C_W) - V_{Wi} \frac{\partial C_W}{\partial x_i} = \phi S_W \frac{\partial C_W}{\partial t}$$

3

soil phase

$$\frac{dC_S}{dt} = \lambda_{SW} [K_{SW} C_W - C_S] + \lambda_{SO} [K_{SO} - C_S]$$

4



and oil phase

$$\frac{dS_o}{dt}T = \frac{S_v \lambda_{vo}}{\rho_o}(C_v - C_{evo}) + \frac{\rho_s S_o \lambda_{so}}{\rho_o}(C_s - K_{so})$$

$$+ \frac{S_w \lambda_D}{\rho_o}(C_w - C_{ew})$$

5

In Equations 2 through 5 the subscripts v, w, s and o refer to the vapor, water, soil and oil phases respectively. The variables and parameters in Equations 2 through 5 are defined as:

- C is the VOC concentration (M/L³)
- C* is the VOC concentration in the source/sink (M/L³)
- C_{ev} is the VOC equilibrium vapor concentration (M/L³)
- C_{ew} is the VOC equilibrium water concentration (M/L³)
- H is Henry's Law partition coefficient
- K_{sw} is the soil-water adsorption isotherm constant (L³/M)
- K_{so} is the soil-oil adsorption constant
- q is the source/sink volumetric flux per volume (t⁻¹)
- S is the phase saturation index
- t is the time
- v_i is the fluid velocity in the direction x,y,z (L/t)
- x_i is the direction x,y,z (L)
- φ is the porosity
- ρ is the phase density (M/L³)
- λ is the mass transfer coefficient (t⁻¹)
- D_i is the dispersion tensor (L²/t)

EXAMPLE SIMULATION

The numerical model developed in this study was used to investigate a hypothetical ISV system. This system consisted of an injection and extraction vent separated by 20 meters of soil known to be contaminated with TCE. TCE, as an irreducible oil phase, initially saturated 0.1% of the available pore space. The soil porosity used was 0.30. Prior to vapor extraction the system was assumed to be in equilibrium at 8 C. This condition specifies an initial TCE concentration of .25 g/l and 1.10 g/l in the vapor and water phases respectively. An initial adsorbed soil concentration was specified as 1.25×10^{-4} g/g. The vapor phase and water phase velocities were assumed to be constant throughout the system and equal to 1.5×10^{-1} m/day and zero respectively. The mass transfer coefficient was taken as 1.0×10^{-1} day⁻¹ and the vapor phase dispersivity coefficient used was 1×10^{-2} m. Values of the Henry's law coefficient and soil-water partition coefficient of 0.24 and 0.2 ml/g respectively were used. Figures 2, 3, 4 and 5 illustrate a continuous record of the TCE concentrations with time at the extraction vent for the oil, vapor, water, and soil phases. Figure 2 shows a linear decrease in oil saturation until 37 days. At this time all TCE in the liquid hydrocarbon phase within the 20 m long system has been dissipated. Figures 3, 4 and 5 show a concentration response in each phase to a changing oil phase saturation. In the vapor phase the TCE concentration drops quickly to a plateau created by a balance between the quantity of TCE supplied to the vapor phase by mass transfer from the oil and water

phases and the quantity of TCE removed by the vapor extraction process. This "equilibrium" condition persists until the oil saturation has been depleted (in this case at 37 days). After the oil saturation has been depleted the vapor phase concentrations are supplied by mass transfer from the water phase only. The abrupt drop in phase concentration as a result of oil phase depletion is observed numerically in the water and soil phases as shown in Figures 4 and 5. The numerical model was also used to investigate the influence of venting schedules on phase concentrations for two conditions, when an oil phase is present and when it is not. Figure 6 investigates the former case and illustrates a venting schedule which incorporates 10 day increments of vapor extraction followed by 10 days of system shutdown. As shown in this figure the vapor phase concentrations are strongly influenced by the change in extraction rate. As a result of TCE vaporizing from the oil, the vapor concentration approaches its pre-extraction concentration levels. Figure 7 similarly illustrates a venting schedule for the case where all the oil phase has been dissipated. The concentration recovery with respect to the pre-extraction level is very slight. The type of information contained in Figures 2 through 7 can be applied to any ISV system. Changes in ISV system performance can be predicted for site specific studies using the numerical model developed in this study. Estimates of the time required to achieve site cleanup using different configurations in vent length and spacing, and extraction rate and schedule can be made prior to system installation.



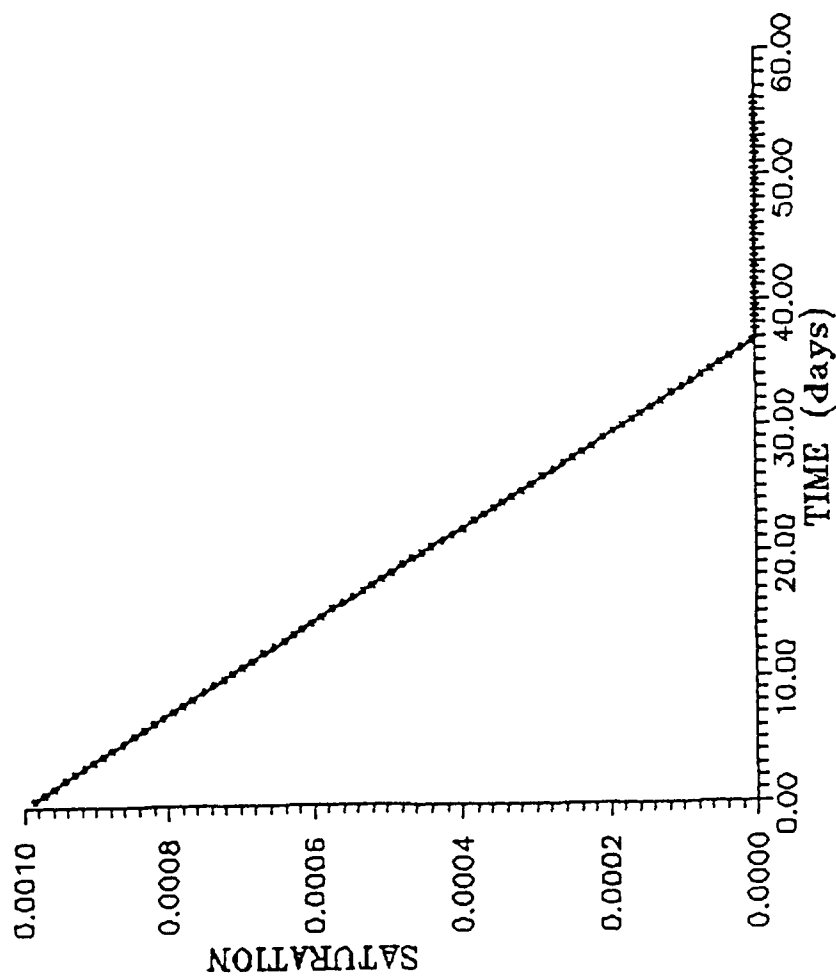


FIGURE 2. Change in TCE Oil Saturation at the Extraction Vent
Under conditions of constant extraction rate the oil
saturation declines linearly with time until depletion
occurs (in this case at 37 days of system operation).

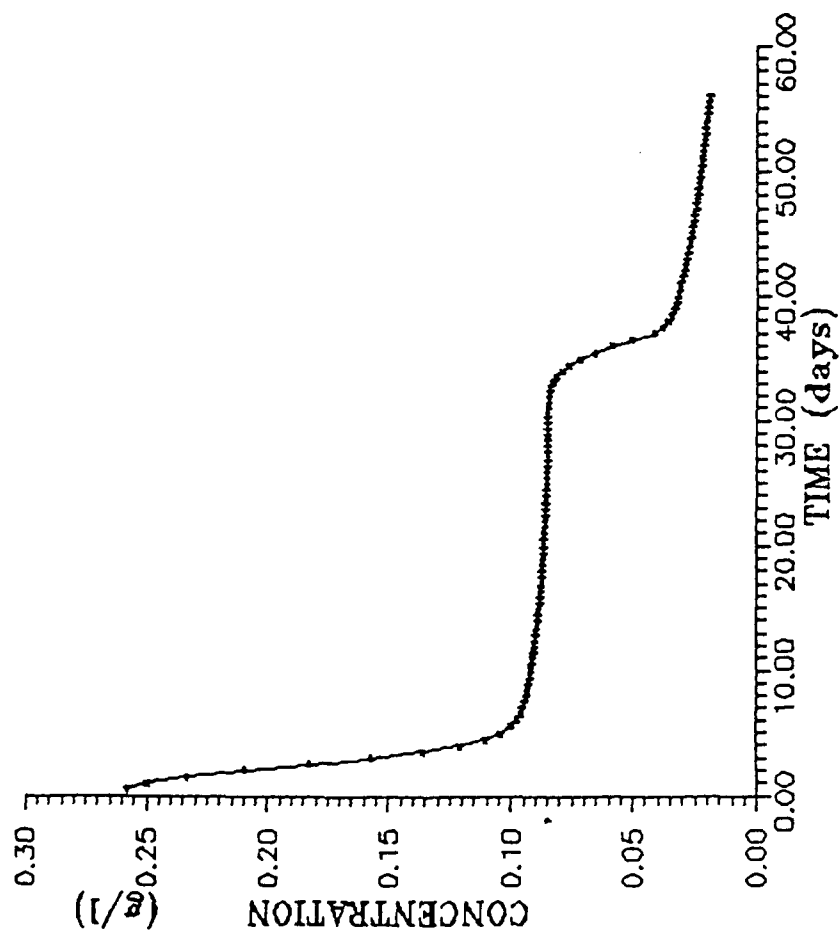


FIGURE 3. Change in TCE Vapor Concentration at the Extraction Vent Under conditions of constant extraction rate the vapor concentration declines rapidly until a plateau is reached. The vapor concentration remains at the plateau level until the oil phase is depleted and then sharply declines (in this case at 37 days of system operation.)

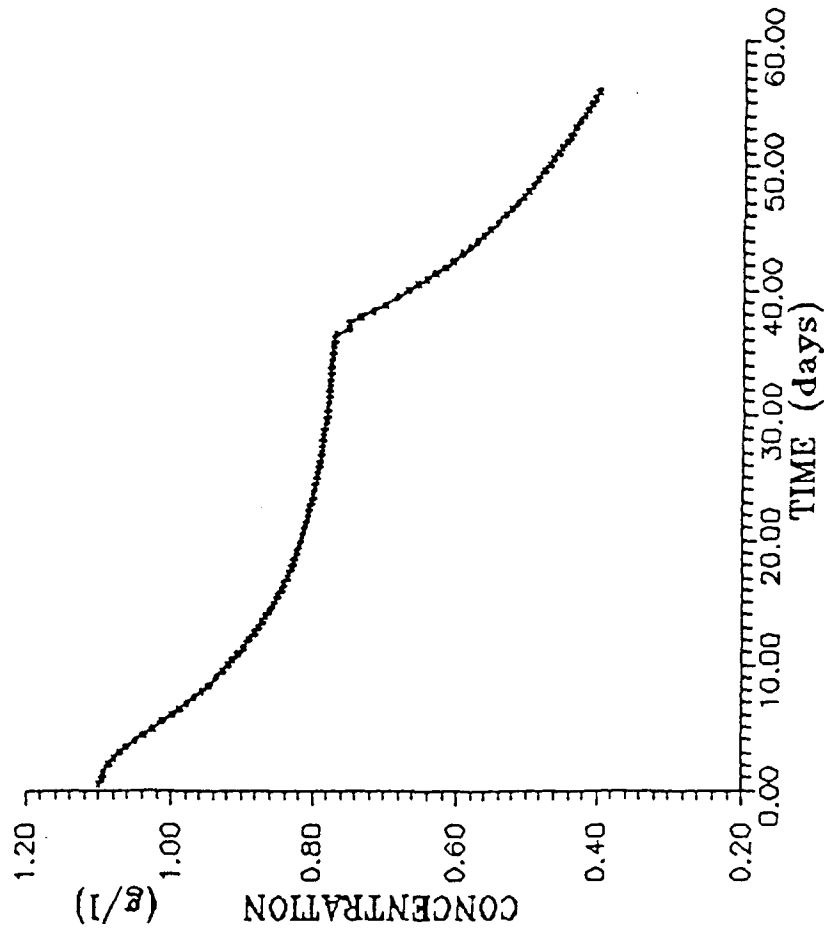


FIGURE 4. Change in TCE Water Concentration at the Extraction Vent
 Under conditions of constant extraction rate the
 water concentration declines until a plateau is
 reached. The water concentration remains at the plateau
 level until the oil phase is depleted and then sharply
 declines (in this case at 37 days of system operation.)

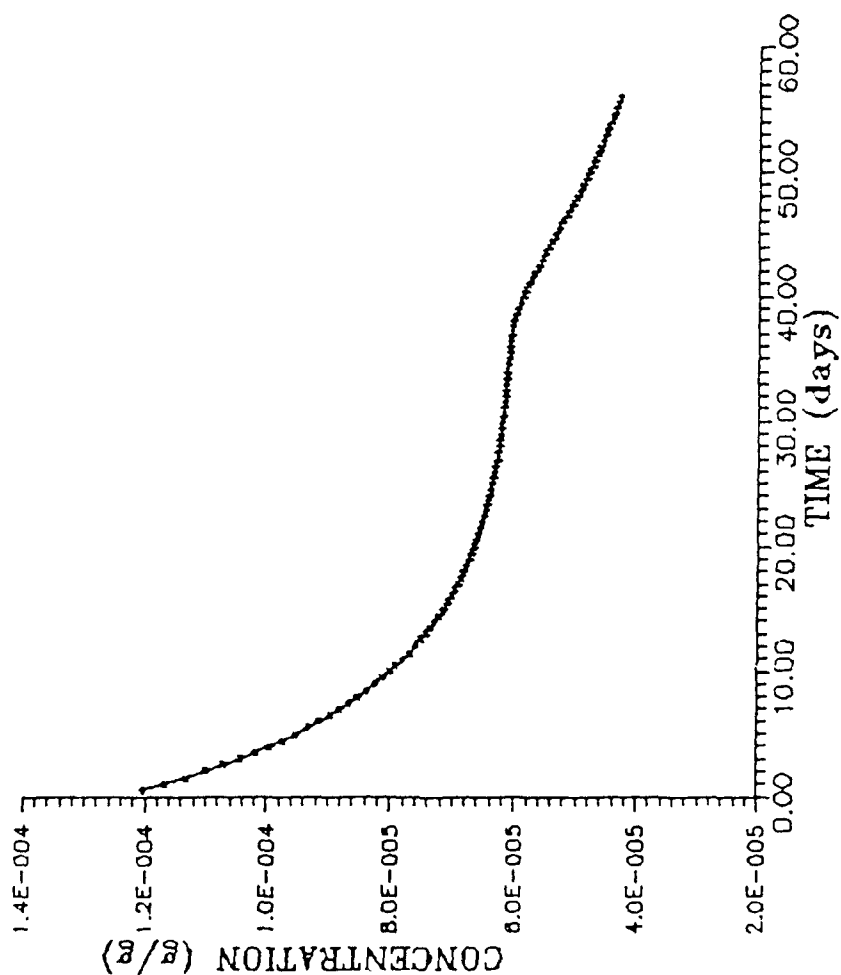


FIGURE 5. Change in TCE Soil Concentration at the Extraction Vent Under conditions of constant extraction rate the soil concentration declines until a plateau is reached. The soil concentration remains at the plateau level until the oil phase is depleted and then sharply declines (in this case at 37 days of system operation.)

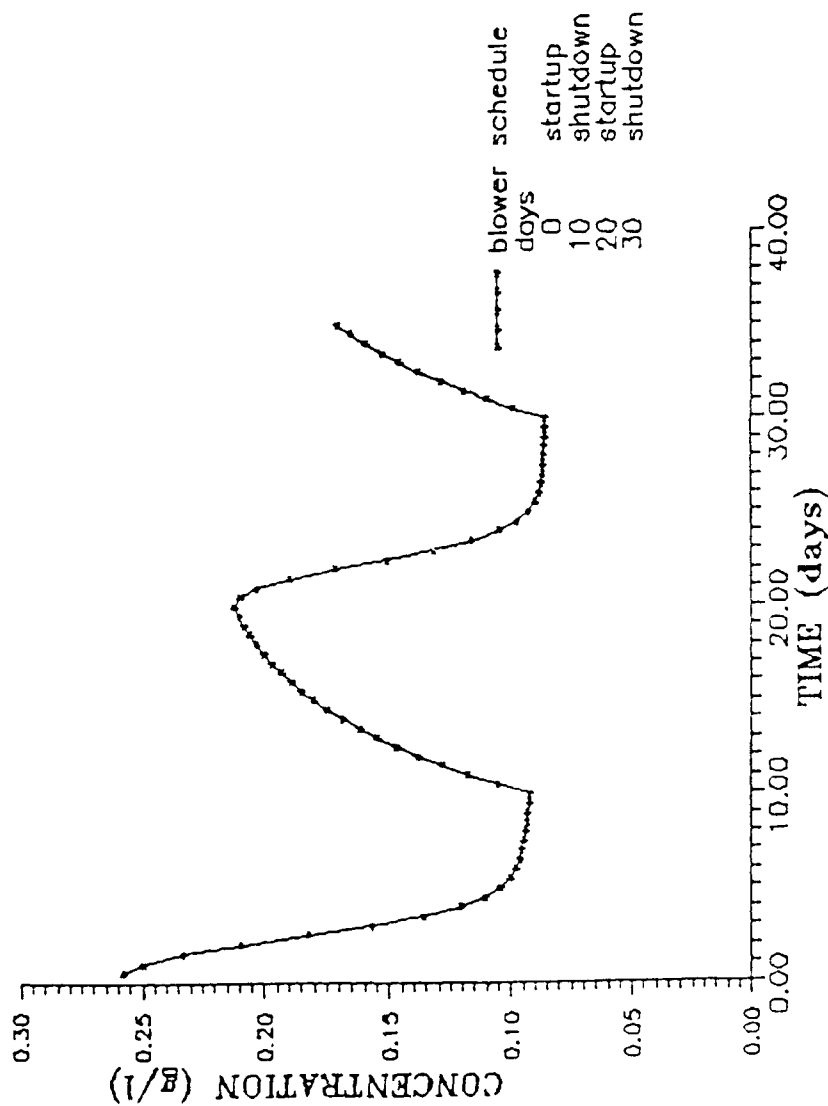


FIGURE 6. Change in TCE Vapor Concentration at the Extraction Vent
 Under conditions of on/off venting the vapor concentration undergoes large changes in concentration. In the presence of an oil phase the vapor concentration will approach the pre-operation concentration levels. reached.

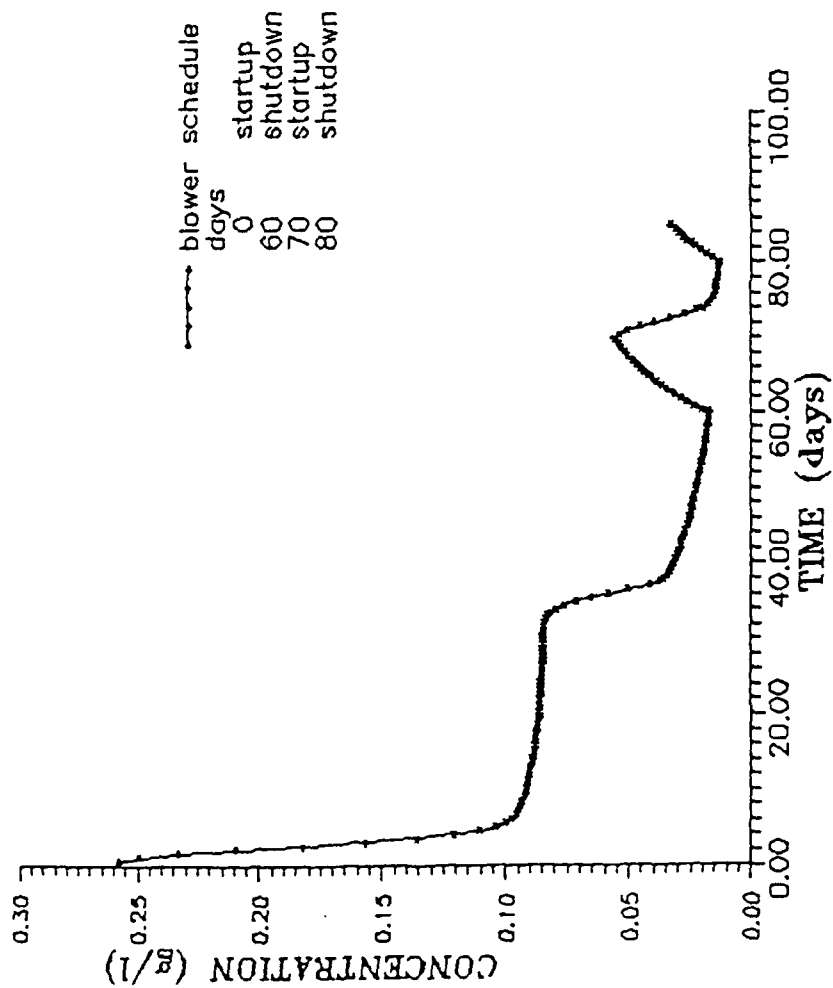


FIGURE 7. Change in TCE Vapor Concentration at the Extraction Vent
 Under conditions of on/off venting the vapor concentration undergoes large changes in concentration. In the absence of an oil phase the vapor concentration will not approach the pre-operation concentration levels. reached.

TCAAP SITE D SIMULATION

The three-dimensional code developed in this study was applied at TCAAP Site D using the available site specific data. The compressible gas code CSUGAS (Eisenbeis et al. 1989) was used to simulate flow-field velocities. Water phase velocities within the unsaturated zone were considered negligible in comparison with the gas phase velocities and therefore treated as being equal to zero. The intrinsic soil properties and initial VOC content were obtained from Anastos (1985). The VOC production rate and ISV system operational history are contained in Wenck (1988) and Weston (1990). Approximately 1500 days of Site D ISV operational history were simulated. The numerically determined VOC production at Site D agreed, within a few to several per cent, with the operational data.

TCAAP is a government owned contractor operated facility. The primary responsibilities of the installation were to manufacture small arms ammunition and related materials. Disposal operations began at Site D in 1949 or 1950 and continued intermittently through the early 1970's. Among the chemicals disposed were scrap propellant, primer, thinner and varnish, solvent, oil and grease. These chemicals were dumped and sometimes burned at Site D.

Biang et al. (1988) summarize the local geology in the vicinity of Site D as being comprised primarily of a brown-gray, fine to coarse silicate sand (termed the Arsenal and Hillside Sands) which extends to a depth of approximately 430 feet below the ground surface. The sand is underlain by the Jordan Sandstone.

Weston (1985) describes the unconsolidated sediments found at Site D as primarily sands with some gravel. Based on tests performed on four near surface borings the physical properties of the soil were determined. The dry density of the soil is approximately 102 pounds per cubic foot (pcf) and has a porosity of approximately 39%. The water content and water saturation are approximately 4% and 14%, respectively. The hydraulic conductivity of the sand is reported to range from 5.7×10^{-4} to 3.5×10^{-3} cm/sec (Weston 1990). Groundwater at Site D was encountered within the Hillside Sand at a depth of approximately 168 feet below the ground surface.

Weston (1985) reports chemical analyses performed in 1984 on 131 soil borings at TCAAP. The 43 soil borings analyzed at Site D all contained VOC contamination between approximately 50 and 8,000 parts per million (ppm). Trichloroethylene (TCE) was found in all borings at Site D. It comprised over 70% of the reported contamination and is considered the principal contaminant. 1,1,1-trichloroethane (TCA) was determined to represent approximately 20% of the contamination due to VOC. Three additional soil borings were performed in 1987 after approximately 1 year of ISV treatment. One identified detectable TCE at 152 feet below ground surface. Shallow soil samples found no evidence of VOC. In addition to these chemical analyses Weston 1990 conducted chemical analyses on seven additional soil borings. These borings were completed during May 1990 after approximately three years of ISV treatment to 30 feet below the ground surface and located in areas previously identified as having VOC contamination. The results of these tests indicated that the post treatment concentration levels had been

reduced by four to five orders of magnitude compared to the earlier sampling. Figure 8 illustrates a plan view of the Site D ISV system. It consists of 39 vents screened to approximately 34 feet below the ground surface, an air collection manifold and four centrifugal blowers. In addition, a clay cap was installed at Site D in late 1985 after soils exhibiting PCB contamination were excavated. A full scale ISV system was installed at Site D and operation began in February 1986. In early March the system was shut down for approximately five months and resumed operation in July 1986. With the exception of a few infrequent interruptions, the system has been in almost continuous operation since that time. The air extraction rate since startup in July 1986 has averaged approximately 5,800 cfm. Since the start of ISV remediation at Site D through June 1990, over 108,000 pounds of contaminant have been vapor extracted from Site D (Weston, 1990).

To perform the numerical simulation Site D was discretized into a $22 \times 28 \times 8$ ($N_X \times N_Y \times N_Z$) grid totaling 4,928 finite-difference cells. Grid dimensions vary from 5 feet at the extraction vents to 40 feet near the horizontal boundaries. In the vertical direction the grid dimensions vary from 2 feet for the clay liner to 50 feet near the water table which occurs at approximately 168 feet below the ground surface. Recognizing that over 70% of the known contaminants at Site D are TCE; the single component modeled in the numerical exercise was TCE. As illustrated in Figure 1, the VOC may exist in the oil, water, vapor and soil adsorbed phases. Using the available data (Anastos, 1985) an initial phase partitioning estimate of approximately 104,000

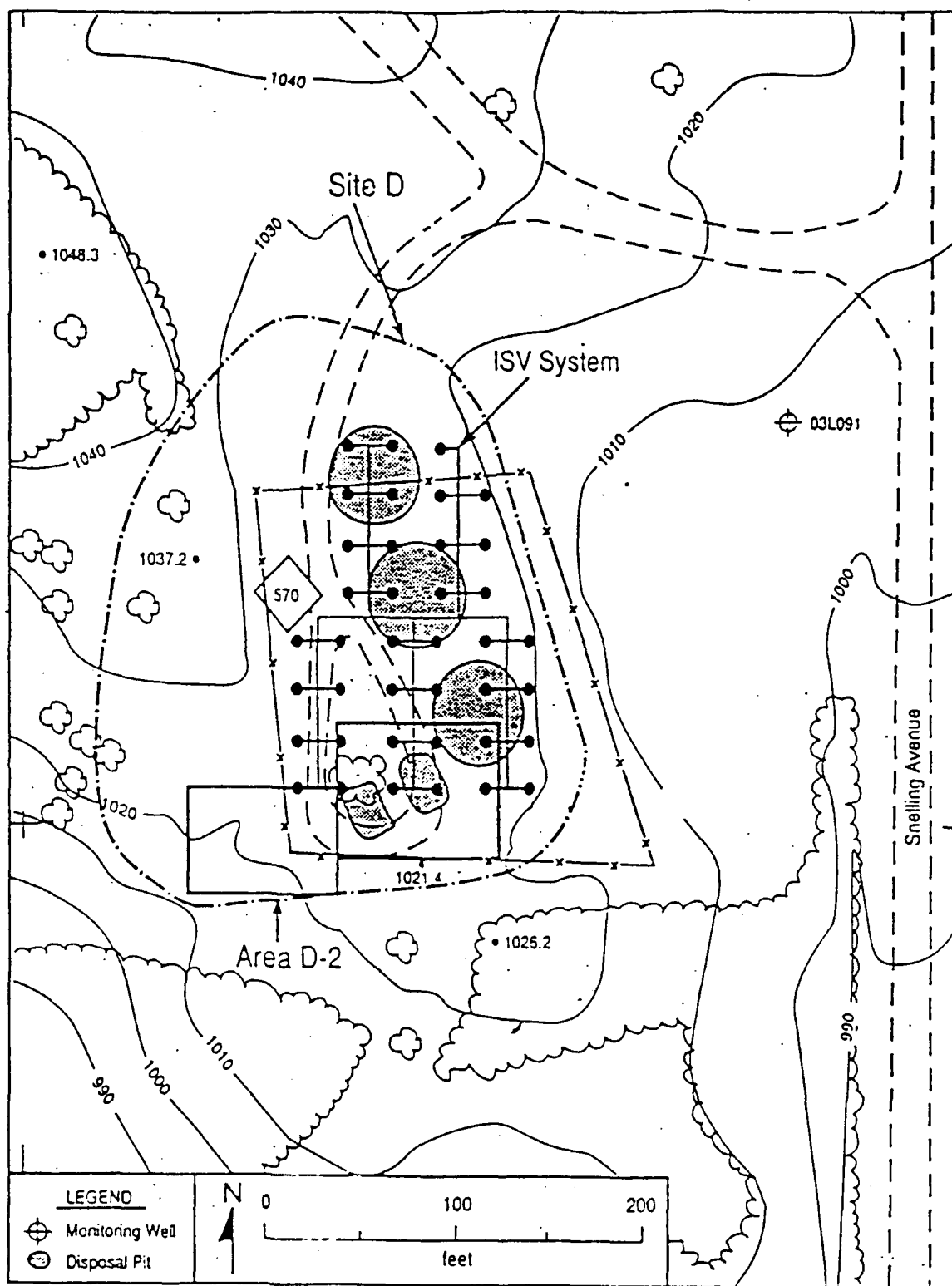


FIGURE 8 In-Situ Volatilization System at Site D (Source: Modified from ANL 1988)

pounds of VOC in the oil phase, 7000 pounds of VOC in the vapor phase and 14,000 pounds of VOC in the water phase was made. The total initial VOC content of Site D was, therefore, estimated to be approximately 124,000 pounds.

Figure 9 illustrates the cumulative VOC production with time at Site D. The data plotted is obtained from Wenck (1988) and Weston (1990) and represents the total production from system startup through June 1990. The time in days represent days of system operation. The cumulative total shows a steady decrease in production rate. During the first 500 days of system operation, approximately 75,000 pounds of VOC were produced. In the second and third 500 day periods approximately 20,000 and 10,000 pounds of VOC were produced, respectively. The cumulative total through June 1990 was approximately 108,000 pounds. Figure 9, therefore has two types of information, total VOC production in the 1500 day period of operation and trends in VOC production represented by a systematic decrease over time. Figure 10 illustrates the numerically obtained solution to VOC production at Site D. This solution was obtained using values for the kinetic rate constants and longitudinal dispersivity of 3×10^{-4} (1/min.) and 0.1 feet, respectively. A comparison of Figures 9 and 10 shows that both exhibit the same trends in VOC production and tend to similar values at 1,450 days. Figure 10 reproduces the Site D production data during the first 500 days almost exactly with a difference of less than 1% total mass. During the period 500 to 1,000 days, Site D data reports 94,000 pounds of VOC while the numerical solution predicts 102,000 pounds, an overestimate of

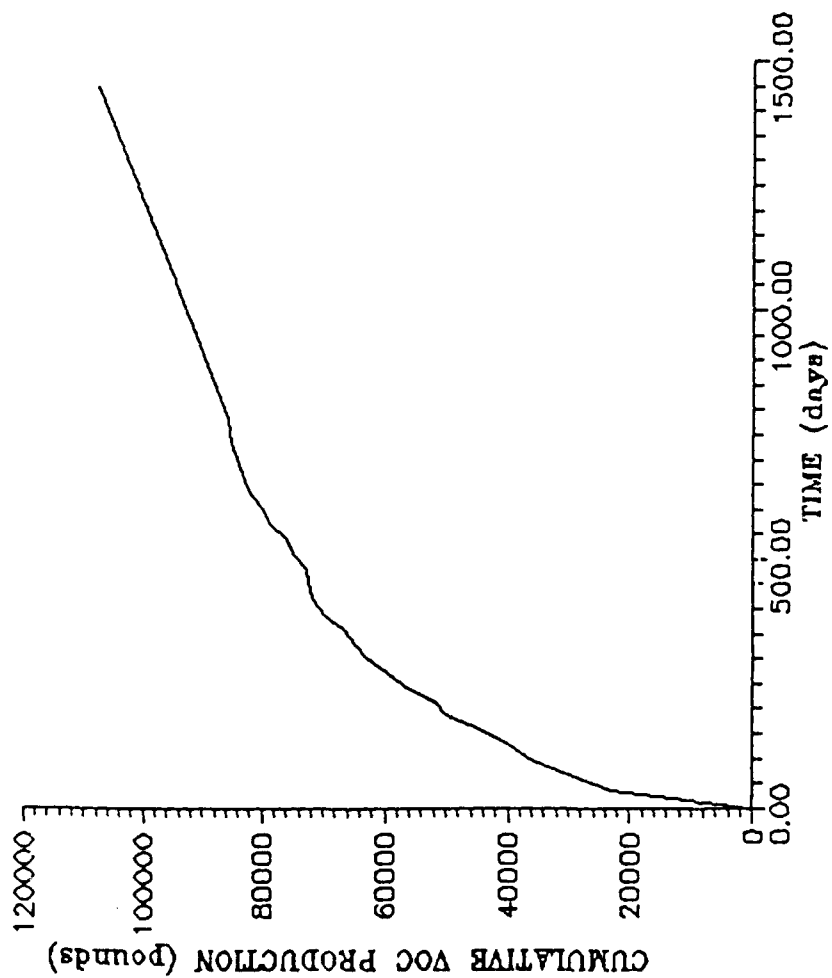


FIGURE 9. Cumulative VOC Production at TCAAP Site D

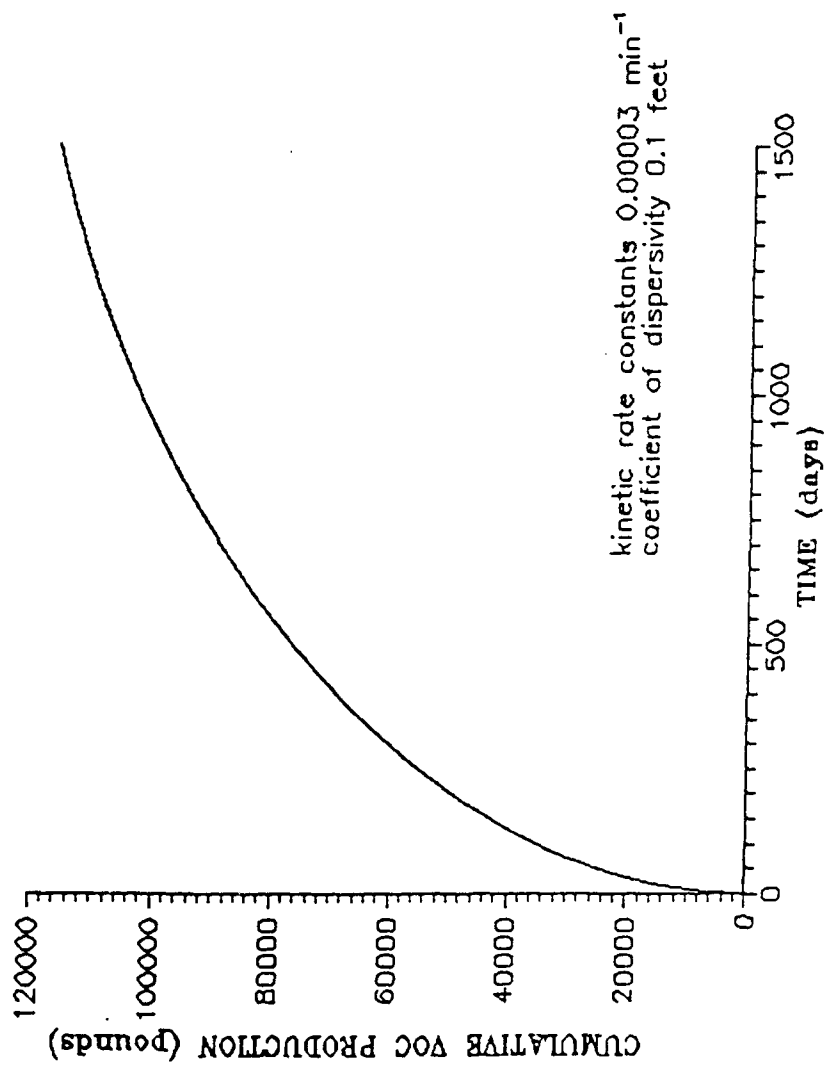


FIGURE 10. Numerically Calculated VOC Production at TCAAP Site D

8,000 pounds. This discrepancy represents a difference of 8.7%. At 1,450 days TCAAP data shows 106,000 pounds and the numerical solution again overestimates by 8,000 pounds and predicts 114,000, a difference of 7.5%. The source of this disagreement may be due to inaccurate parameter estimation, smoothing the air extraction rate, inaccurate characterization of soil and flow properties, incorrect initial soil contamination specification, approximating a multi-component hydrocarbon as a single component or inaccurate field measurements of the data.

SUMMARY AND CONCLUSIONS

This study developed a three-dimensional numerical model for determining the multi-phase fate and transport of volatile organic compounds in unsaturated soils. The model requires a companion simulator which calculates air phase and water phase velocities. The code was designed to investigate ISV remediation systems and is currently run on an IBM PC/2.

The model in this report can be used to help design ISV remediation systems. This numerical tool enables a pre-construction prediction for the number, length and spacing of extraction vents required to achieve the desired cleanup after a specified time of system operation. In addition the model developed in this report was used to replicate operational data from an existing ISV remediation system at the Twin Cities Army Ammunition Plant near New Brighton, Minnesota. The operational data consisted of approximately 1,500 days of VOC production data.

Both the trend in VOC production rate and the total cumulative production were closely reproduced.

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IDENTIFICATION AND EVALUATION OF INTERIM ACTION TECHNOLOGIES OF THE M-1 PONDS AT THE ROCKY MOUNTAIN ARSENAL

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Abstract

The M-1 Settling Basins in the Rocky Mountain Arsenal (RMA) were constructed to treat waste fluids from a lewisite production facility. Several investigations have found that the contaminants in the basins are primarily arsenic (about 4.5 percent) and mercury (about 0.5 percent), with the bulk of the material being oxides or carbonates of calcium. The Federal Facility Agreement for the Rocky Mountain Arsenal specified the M-1 Settling Basins area as one of several sites to be addressed by Interim Response Action (IRA). As the preliminary step in identifying IRA alternatives, potentially applicable technologies were identified, described, and evaluated in terms of their feasibility and general effectiveness. Acceptable technologies or combination of technologies were developed into the IRA alternatives. Eight alternatives were developed as IRAs for the M-1 Settling Basins: no action; monitoring; institutional controls; slurry wall with cap; multilayered cap; in-situ vitrification; chemical fixation with onsite storage; and chemical fixation with offsite disposal. These alternatives were then evaluated with respect to: overall protectiveness of human health and the environment; compliance with Applicable or Relevant and Appropriate Requirements (ARARs); reduction in mobility, toxicity, or volume; short- and long-term effectiveness; and implementability. An in-situ vitrification (ISV) engineering-scale treatability test was performed as part of this assessment in the summer of 1989. The ISV process uses electrical energy to melt inorganic materials (e.g. soil) for the purpose of thermochemically treating free and/or containerized contaminants present within the treatment volume. In soil, the process simultaneously destroys and/or removes organic contaminants while chemically incorporating (immobilizing) inorganic contaminants into a chemically inert, stable glass and crystalline residual product. The Final Decision Document for the M-1 Settling Basins recommended ISV as the preferred interim response action at the site.

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INTRODUCTION

This paper will present the IRA objective and identify potential interim response action technologies specific to the M-1 Settling Basins at RMA. As the preliminary step to identifying IRA alternatives, potentially applicable technologies for the IRAs were identified, described, and evaluated in terms of their feasibility and general effectiveness. Acceptable alternatives were developed into the IRA alternatives presented in the paper.

SITE DESCRIPTION

The RMA occupies more than 17,000 acres (approximately 27 square miles) in Adams County, located northeast of metropolitan Denver, Colorado (Figure 1). The property was purchased by the U.S. Government in 1942 for use during World War II to manufacture and assemble chemical warfare materials, such as mustard and lewisite, and incendiary munitions.

The M-1 Basins are located in the South Plants area just south of December 7th Avenue along the northern edge of the northwest quarter of Section 1.0 (Figure 2). The northwest corner of the basins is 75 feet south of the centerline of December 7th Avenue and 25 feet east of the contaminated sewer line that drained from the South Plants into the Lime Settling Basins. The elevation of the ground surface in the M-1 Basins area is approximately 5,265 feet above mean sea level (MSL). The basins and the berms surrounding them, all of which are now buried and partially built upon, occupy an area of approximately 46,200 square feet.

History

Two basins were originally constructed in 1942, but when these filled with solids, a third was constructed in 1943. All three were unlined, each measured approximately 90 feet wide (E-W), 115 feet long, and 7 feet deep, according to the as-built drawings. They were initially constructed to treat waste fluids from the lewisite (an Arsenic-based blister agent) disposal facility. However, lesser amounts of waste materials from alleged spills within the acetylene generation building, the thionylchloride plant, and the arsenic trichloride plant may have been routed through floor drains and the connecting piping to the basins (Ebasco Services, Inc. 1987).

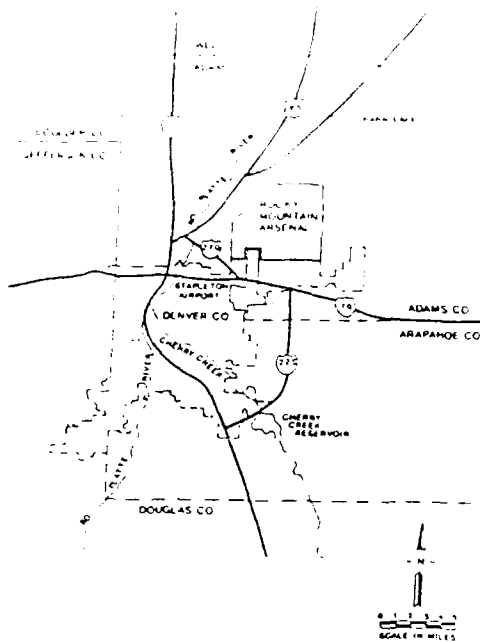


FIGURE 1
ROCKY MOUNTAIN ARSENAL
LOCATION MAP

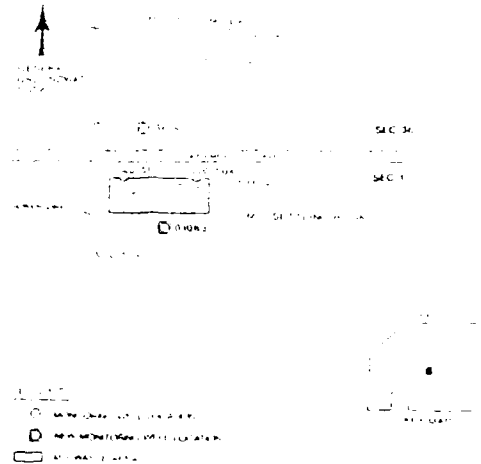


FIGURE 2
M-1 SETTLING BASINS
LOCATION MAP

01524 01083
1209

W00-7
1211

W00-8
1209

01511
1211

34 193

1000000
1211

M-1 BASINS

1000000
1211

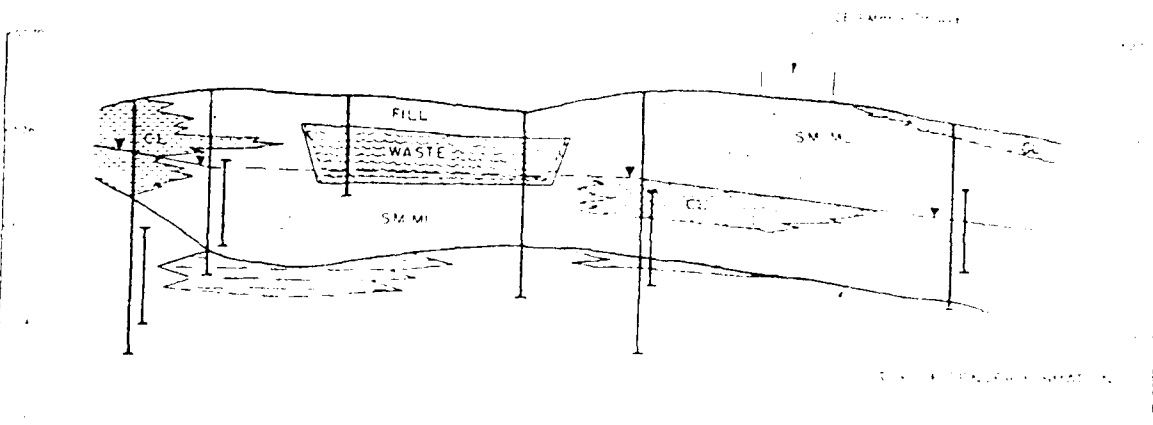


FIGURE 3
M-1 SETTLING BASINS GENERALIZED CROSS SECTION

The liquids discharged into the basins first passed through a set of reactor towers where calcium carbonate was added, then through a wooden trough into the M-1 Settling Basins where the arsenic precipitated out of solution. The elutriate was decanted off through an 18-inch-diameter pipe to the Lime Settling Basins (in Section 36) where final treatment occurred and then routed into Basin A (Ebasco Services, Inc. 1987).

The basins also received a considerable amount of mercuric chloride catalyst, possibly from a spill. Various sources reported quantities such as 183,000 pounds, 500 pounds, 30,000 gallons, and \$25,000 worth (Ebasco Services, Inc. 1988).

The basins were backfilled, probably in 1947, and are now covered with soil and/or structures. The facilities that surround the M-1 Basins area were used in the manufacture of bicycloheptadiene (an organic chemical used in the manufacturing of pesticides) until 1974.

Geology

The M-1 Basins are located on a paleotopographic high near the headwaters of a series of paleodrainages that originate in the upland area occupied by Section 1.0. Two significant stratigraphic units have been identified at the site. These are the Quaternary Alluvium and the Cretaceous-Tertiary Denver Formation.

The surficial materials in the M-1 Basins are 10 to 15 feet thick and overlie the Denver Formation. The entire area around the basins is covered with a veneer of imported soil. The soil cover over the waste material in the basins ranged from 1.5- to 4.5-feet thick.

The unconsolidated alluvial soil overlying the Denver Formation bedrock is composed of fine- to medium-grained, subangular, alluvial, and eolian, silts, and clays, with some minor amounts of gravel.

The Denver Formation is generally composed of finer grained materials including interbedded claystones, siltstones, and sandstones with some interbedded lignite seams. The contact between the alluvial unit and the Denver Formation is generally characterized by a claystone;



however, it may also be marked by siltstone or lignite (Figure 3). In the M-1 Basins area the contact between the alluvium and the Denver formation was found between 9 and 14 feet below the ground surface.

Site Hydrology

In the M-1 Basins area, groundwater flow in the alluvial aquifer is apparently toward the north and possibly slightly northwest due to the influence of localized mounding of groundwater in the South Plants area. The local groundwater gradient is in the range of 0.008 to 0.011 ft/ft. Due to seasonal variations and local topography, the top of the groundwater ranges from approximately 5 to 10 feet below ground surface. The lower portions of the sludge are an inundated part of the year due to these fluctuations. The average saturated thickness of the alluvial aquifer is approximately 8 feet.

M-1 BASIN CONTAMINATION

Soils and Sludge

Soil samples collected and analyzed during investigations of the M-1 Settling Basins indicated high concentrations of arsenic and mercury in the soil in and around the basins at depths of 0.5 foot to approximately 7.0 feet. The concentration of arsenic and mercury in samples taken within the basins was variable and ranged from 0.01 to 11.0 percent. Table 1 shows a summary of the contaminants found in soil and sludge samples taken during the field investigations.

TABLE 1
M-1 SETTLING BASINS
CONTAMINANTS

Contaminant	Soil ($\mu\text{g/g}$)	Sludge ($\mu\text{g/g}$)
As	9.2 - 1,300	17,00 - 110,000
Hg	0.33 - 210	400 - 9,400
VOC*	1.8 - 5,000	0.5 - 600

* Primarily Methylene Chloride and Bicycloheptadiene



Groundwater

Analytical results from groundwater sampling conducted in spring 1989 confirm that there are high levels of arsenic in the groundwater. Total and dissolved arsenic concentrations are quite similar in magnitude and indicate a high concentration of arsenic immediately downgradient of the M-1 Settling Basins (Figure 4). The high concentrations of arsenic downgradient of the M-1 Settling Basins clearly indicate that this site is a direct source of arsenic contamination to the groundwater.

Organics Fate and Transport

Although the sludge material and the overburden soil at the M-1 Settling Basins contain several organic compounds in trace amounts, two organic compounds are present in concentrations as high as four orders of magnitude above their detection limits: bicycloheptadiene and dicyclopentadiene. Both are from an upgradient site and appear to be sorbed on to the sludge material and on to the local silty sands. During periods of high groundwater, the compounds are desorbed into the alluvial groundwater and are transported downgradient.

Metals Fate and Transport

The primary metal contaminants of concern at the M-1 Settling Basins are arsenic and mercury. The contaminant assessment report also showed occasional, isolated, elevated concentrations of cadmium. The metals are transported downgradient by the flow of groundwater at various rates.

EVALUATION BASIS FOR INTERIM RESPONSE ACTIVITY

This section summarizes the engineering constraints considered in the technology and alternative evaluation process.

The total areal extent of the three M-1 Settling Basins is shown to be 115 feet by 300 feet on design drawings. The sludge material in the basins extends to a depth of 7 to 8 feet below

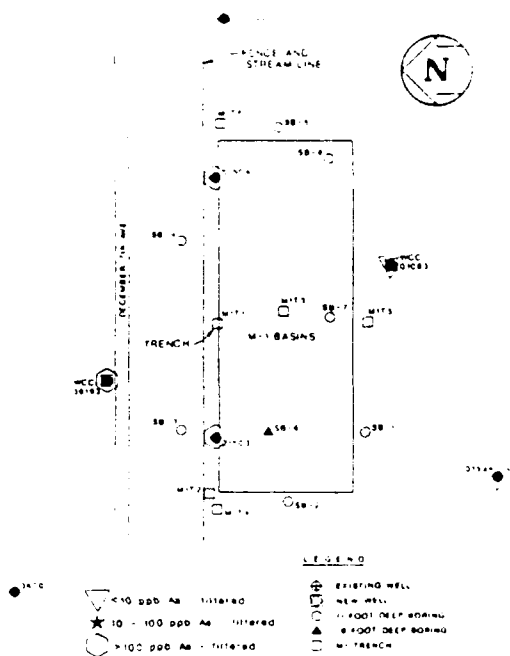


FIGURE 4
M-1 SETTLING BASINS
SAMPLING PROGRAM

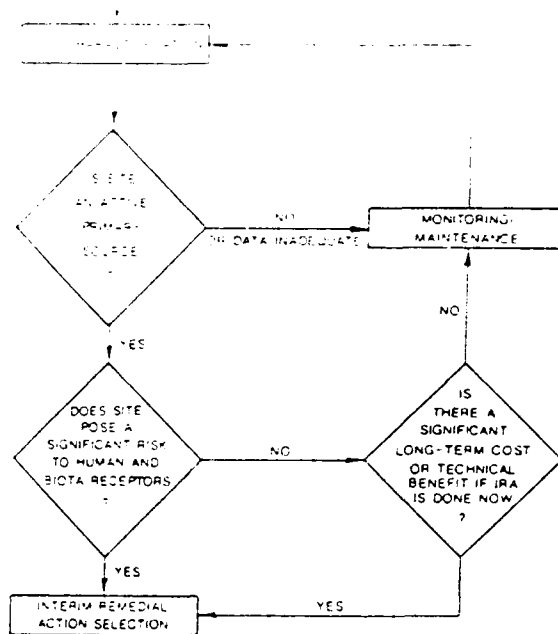


FIGURE 5
DECISION FLOW CHART FOR IRAs

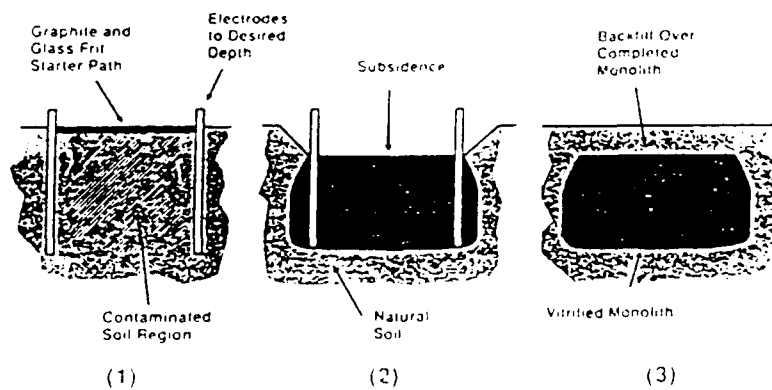


FIGURE 6
STAGES OF ISV PROCESSING

ground surface and is covered by 0.5 to 4.5 feet of soil overburden. The total volume of the sludge is estimated to be approximately 6,400 yd³.

Preliminary analysis of the sludge in the basins indicates that the in-place waste is approximately 47 percent water. The sludge is described as a gray-to-white very wet, silty clay-like material, similar to the consistency of toothpaste. Based on investigations, this material is assumed on the average to be about 4.5 percent arsenic, 0.5 percent mercury with the balance being calcium oxide or calcium carbonate as measured on a dry basis. The wet density of this material is assumed to be 1.35 tons/yd³.

The natural and imported soil surrounding the basins is gravelly to silty sands, with lesser amounts of clayey sands to silty sand. The in-place density of this soil is assumed to be 1.5 tons/yd³.

A summary of the technical evaluation basis is shown in Table 2.

PURPOSE OF THE INTERIM RESPONSE ACTION (IRA) ALTERNATIVE ASSESSMENT

The goal of the assessment document was to evaluate alternatives based upon, but not limited to, factors such as the protection of human health and the environment; compliance with ARARs; reduction in mobility, toxicity, volume; short- and long-term effectiveness; and implementability. Consistent with the Comprehensive Environmental Response, Compensation and Recovery Act of 1980 (CERCLA), as amended by SARA, 1986, and the National Contingency Plan (NCP), the assessment seeks to balance preferences for treatment on site and for responses that permanently reduce the mobility, toxicity, or volume of hazardous substances against the need, in the context of removal actions, for consistency with the final remedy and for responses that are practical, cost-efficient, and that reduce or control hazards posed by the site as early as possible.



TABLE 2
M-1 SETTLING BASINS
EVALUATION BASIS

Site Characteristics

	<u>Units</u>	<u>Estimates</u>	<u>Maximum</u>
Perimeter	ft	830	910
Surface Area	ft ²	34,500	46,200
Depth of Contamination	ft	7	10
Depth of Groundwater	ft	8-9	10
Depth of Confining Layer	ft	18	18
Volume	yd ³		
Sludge		6,400	6,400
Soil		2,600	10,700
Total		9,000	17,100

Sludge Characteristics

Gray-to-white, very wet silty clay
like material
Density: 1.35 tons/yd³

Soil Characteristics

Gravelly-to-silty sands, with lesser amounts of
clayey sand to silty sand
Density: 1.5 tons/yd³

<u>Contaminant</u>	<u>Soil Geometric Mean (ug/g)</u>	<u>Sludge Geometric</u>
<u>Mean (ug/g)</u>		
Volatile Organic Compounds/GCMS		
Methylene Chloride (CH ₂ CL ₂)	3.5	3.7
Bicycloheptadiene (BCHPD)	235	45
Semivolatile Organic Compounds/GCMS		
Aldrin (ALDRN)	8	
Dicyclopentadiene (DCPD)	1340	8
Dieldrin (DLDRN)	4	
Hexachlorocyclopentadiene (CL6CP)	3000	
Isodrin (ISODR)	10	
Metals/ICP		
Cadmium (Cd)	3.6	22.9
Chromium (Cr)	11.9	9
Copper (Cu)	12.6	17.7
Lead (Pb)	26.5	42.7
Zinc (Zn)	61	35.1
Separate Analyses/AA		
Arsenic (As)78	38300	
Mercury (Hg)	6	2550



IRA CANDIDATE SELECTION CRITERIA

To evaluate whether and what type of response action is necessary and appropriate, the following questions have been developed as part of a decision logic (Figure 5):

- (1) Is the site an active primary source?
 - Is it an active source of groundwater contamination?
 - Is it a primary groundwater contamination source?
- (2) Does the site pose a significant risk to human or biota receptors?
 - Have potential receptors been identified?
 - Have previous studies been confirmed by new data?
 - Is there any conflicting evidence?
- (3) Is there a significant long-term benefit if an IRA is done now?
 - Will interim action result in an accelerated cleanup?
 - Will interim action reduce long-term costs?

The M-1 Settling Basins have been evaluated as being an active primary source of groundwater contamination. Although this site does not appear to pose a significant risk to human or biota receptors at this time, there was both a long-term cost and technical benefit in performing an IRA now since delaying treatment would allow arsenic to spread and make final remediation both more costly and complex insofar as a larger area must then be addressed.

INTERIM RESPONSE ACTION ALTERNATIVES

Eight alternatives were developed as interim response actions (IRAs) according to Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA), as amended by SARA, 1986, guidance (Environmental Protection Agency 1988). The suite of alternatives includes administrative, containment, treatment, and temporary storage/disposal options. The alternatives were:

<u>Alternative</u>	<u>Description</u>
1	No action
2	Monitoring
3	Institutional controls
4	Slurry wall with cap
5	Multilayered cap
6	Chemical fixation with onsite storage
7	Chemical fixation with offsite disposal
8	In-situ vitrification

Alternative 1 - No Action

This alternative assumed that no action would be taken to contain or treat contaminated soils and sludge at the M-1 Settling Basins. Additional groundwater monitoring would not be required if this alternative was selected.



Alternative 2 - Monitoring

This alternative assumed that the only action taken at the M-1 Settling Basins would be additional groundwater monitoring. This monitoring would track the continuing effect of the M-1 Settling Basins on the alluvial aquifer. In addition, monitoring will be part of Alternatives 3 through 8. The monitoring consisted of quarterly sampling and analysis of groundwater from existing monitoring wells. The water will be analyzed for the following analytes:

- Volatile halogenated organics
- Volatile aromatic organics
- Semivolatile halogenated organics
- Total and dissolved arsenic
- Total and dissolved mercury
- ICP metals
- pH

Alternative 3 - Institutional Controls

The institutional control alternative consisted of constructing a fence around the site. This would entail the construction of approximately 910 lineal feet of chainlink fence with controlled access points (i.e., locked gates).

Alternative 4 - Slurry Wall with Cap

The slurry wall and cap alternative would consist of constructing a slurry wall around the M-1 Settling Basins and a cap covering the area enclosed by the slurry wall. This alternative would enclose the source of contamination and reduce the migration of hazardous constituents. The slurry wall and cap would be designed to restrict the contamination source until a final remedy action is selected and implemented.

Alternative 5 - Multilayered Cap

This alternative would consist of covering the M-1 Settling Basins with a cap to reduce infiltration of surface water. The cap would be designed and constructed to cover the entire basin area. The cap would consist of, from the base upwards, an 18-inch thick compacted clayey soil layer, a 60-mil-thick high-density polyethylene (HDPE) flexible membrane liner, a synthetic drainage net, a geotextile filter fabric, and a 1-foot protective soil layer. The cap would be sloped from the center to the edges at about 2 or 3 percent to facilitate surface water runoff from the cap. This cover design would reduce infiltration of surface water into the M-1 Settling Basins. Water infiltrating the cover would collect onto the clayey soil/flexible membrane composite layer and would be drained to the outside of the cap by gravity through the synthetic drainage net. The geotextile filter fabric would reduce the risk of the synthetic drainage net being clogged by soil particles from the overlying soil layer. Treatment of the protective soil layer, such as cement or asphalt addition, may reduce erosion potential and maintenance of the cover.



Alternative 6 - Chemical Fixation with Onsite Storage

This alternative would include excavation of approximately 10,800 yd³ (9,000 yd³ plus a 20 percent bulking factor) of sludge and soils by sections or subareas to be treated, mixing of the excavated contaminated soils with one or more fixation agents, testing of the treated portions to ensure treatment effectiveness, and placement of the treated soil in an onsite temporary waste pile. This sequence would be repeated for successive subareas until the entire area to be chemically fixed was treated. Two general types of mixing methods are commonly used for the chemical fixation process: batch mixing on the surface of a workpad, or semicontinuous mixing in cement handling equipment, such as a pug mill. The semicontinuous approach was considered more likely to be employed for this remediation.

Chemical fixation is based on treatment methods that surround or encapsulate waste components in a stable inorganic matrix. The treatment additives are selected to accomplish one or more of the following results: reduce the mobility of contaminants by reducing the surface area exposed to leaching fluids, reduce the solubility or toxicity by chemically binding the contaminants into a crystal or inorganic lattice, or solidify or otherwise improve the handling properties of the bulk waste.

The chemically fixed soils and sludges will be temporarily stored in an onsite waste pile. This waste pile would be constructed with a clay liner and cap as well as a synthetic liner, leachate monitoring and collection sump, and groundwater monitoring wells. The fixed soils/sludges must pass leachability tests before they are stored in the waste pile.

Site operations for the chemical fixation process with onsite storage are as follows:

- Excavate contaminated soil, dewater if necessary, and transport to storage pad.
- Convey contaminated soils from the storage pad to the fixation processing equipment.
- Add fixation chemicals and water to the soils and mix to uniformity.
- Transfer the fixed soil to the treatment pad for temporary storage and sampling.
- Backfill the basin area with engineered clean fill.
- Transport fixed soil to the onsite temporary waste pile.

Alternative 7 - Chemical Fixation with Offsite Disposal

Contaminated soils and sludges can be excavated and disposed of offsite in a hazardous waste landfill. Due to the high water content of the M-1 Settling Basin sludges, this material would need to be chemically fixed before it can be placed in a landfill. The sequence of activities that would be performed in this alternative consists of the following:

- Chemical fixation of soil/sludge
- Transportation to offsite landfill



- Site regrading and backfilling of the excavation with clean fill

Alternative 8 - In-situ Vitrification

Contaminated soils and sludge would be vitrified in-situ by introducing sufficient electrical current through the soil to raise the soil temperature to its melting point. The current would be introduced by four electrodes placed in the ground in a square array. A slurry wall will be constructed around the in-situ vitrification (ISV) area. It is assumed that dewatering is unnecessary. The water within the boundaries of the slurry wall will be vaporized during the ISV and water from the surrounding region will not migrate through the slurry wall. The sequence of activities that would be performed in this alternative consists of the following:

- Construction of a slurry wall
- In-situ vitrification in stages throughout the 1-acre site
- Regrade the site

The vitrification process is initiated by the placement of four electrodes in a square array approximately 18 feet apart to a depth of approximately 7 feet (Figure 6). An offgas collection hood will be installed that will route offgases and steam under negative pressure to the offgas control system housed on site in a trailer. A second trailer will house the electrical switchgear that will condition the 4160-volt power obtained from the site power distribution system and deliver it to the electrodes.

The offgas control system will cool, scrub, and filter the vapors collected from the offgassing melt. Assuming this process drives off the 47 percent water fraction of the sludge, approximately 700,000 gallons of water in the form of steam, with trace contaminants of arsenic and mercury, will be generated. This will be condensed indirectly by using a circulating glycol system. Noncondensed acid gases will be absorbed in a packed scrubber column. As a final step in the air pollution control sequence, the exhaust gases will pass through an activated carbon absorber prior to venting to the atmosphere.

The condensate will have elevated concentrations of arsenic and mercury, as well as an alkaline pH. This will require pH adjustment and precipitation of arsenic and mercury to reduce arsenic and mercury levels to accepted discharge limits. Mercury may be in a recoverable form. Actual wastewater treatment will be determined during pilot testing. Any sludge generated in the wastewater treatment will be added to unvitrified soil/sludge for subsequent vitrification. The treated effluent water will be discharged to the alluvial aquifer through a percolation bed.

The process will vitrify the soil/sludge at a rate of approximately 3 to 5 tons/hour. Once the melt is complete, the system will be dismantled and moved to the next area of the vitrification sequence, leaving the melt to cool. To process the approximately 9,000 yd³ of soil, the operation will take about 5 months.



INTERIM ACTION EVALUATION CRITERIA

The interim action alternatives just presented were evaluated based on the following criteria:

- Overall protection of human health and the environment
- Conformance with ARARs
- Reduction of mobility, toxicity, or volume
- Short- and long-term effectiveness
- Implementability

The IRA objectives identified in the Rocky Mountain Arsenal Federal Facility Agreement are included in these criteria. The definition and interpretation of these criteria are outlined below.

Overall Protection of Human Health and the Environment

This criterion assesses whether each alternative provides adequate protection of human health and the environment. Assessment of protection draws upon other evaluation criteria, especially short-term effectiveness and compliance with ARARs and considers whether each alternative poses unacceptable short-term or cross-media impacts.

Conformance with ARARs

One criterion used to evaluate each of the interim action alternatives is compliance with ARARs. Alternatives that meet all ARARs will be preferred because they ensure that interim action will be conducted in a manner that protects human health and the environment.

Reduction of Mobility, Toxicity, or Volume

Reduction of waste mobility, toxicity, or volume reduces the potential of that waste to harm humans or the environment. This evaluation criterion evaluates the process effectiveness to reduce organic and metals concentrations and to reduce waste quantity.

Short- and Long-term Effectiveness

The effectiveness of the interim alternatives was considered in terms of short- and long-term effectiveness in meeting the remedial action objectives.

Short-term effectiveness examines the effectiveness of alternatives in protecting human health and the environment during the construction and implementation period until objectives have been met. Short-term effectiveness has two elements: community protection and worker protection. Community protection considers the risks that results from implementation of the proposed interim action. Worker protection evaluations during interim response activities consider the potential threats that may be posed to workers and the effectiveness and reliability of protective measures that could be taken.



Long-term effectiveness examines the effectiveness of each alternative in maintaining protection of human health and the environment after response objectives have been met. The evaluation is divided with two main criteria: magnitude of residual risk and adequacy and reliability of long-term controls to manage that residual risk.

Implementability

The implementability criterion addresses the technical and administrative feasibility of an alternative and the availability of various services and materials required for its implementation.

ALTERNATIVE EVALUATION

The eight alternatives were evaluated using the criteria described above. Table 3 is a summary of the eight alternatives rated either good or poor for each criterion. (Table 3 represents a summation of the results of the study. A more rigorous approach was used in the Alternatives Assessment document.)

Based on the IRA Decision Flow Chart three alternatives, No action, Monitoring only, and Institutional controls, were inadequate because the site is an active primary source of contamination.

The multilayered cap and the slurry wall with cap alternatives would both meet the short term criteria for effectiveness, implementability, feasibility and protection of human health. The installation of a slurry wall would improve the protection of the environment by greatly decreasing the migration of contaminants from the basins. However, since migration would still occur, both alternatives would increase the volume of potentially contaminated material which would need to be addressed in the final ROD.

The chemical fixation alternatives are similar to the previous two alternatives; however, they would not be protective of human health because the mercury would be only partially fixed as shown in Table 4. The results shown in Table 4 are based on a chemical fixation treatability test of the M-1 sludge. In addition, chemical fixation would not prevent the leaching of the organic chemicals contained in the contaminated material. Removal of the contaminated material poses another potential problem in that the remaining excavation must be backfilled with clean fill material. Due to the seasonal fluctuation of the groundwater table (discussed earlier), a portion of the fill material would become contaminated with organic chemicals from other upgradient sources, thus increasing the volume of material which would need to be addressed in the final ROD.



TABLE 3
M-1 SETTLING BASINS
ALTERNATIVE EVALUATION SUMMARY

Evaluation Criteria	Alternative							
	No Action	Institutional Controls	Monitoring	Slurry Wall With Cap	Multilayered Cap	Chemical Fixation Onsite Storage	Chemical Fixation Offsite Disposal	In-Situ Vittrification
Feasibility	P	P	P	G	G	G	G	G
Protection of Human Health	P	P	P	G	G	P	P	G
Protection of Environment	P	P	P	G	P	P	P	G
Compliance with ARARs	P	P	P	P	P	P	P	G
Reduction in Mobility	P	P	P	P	P	P	P	G
Reduction in Toxicity	P	P	P	P	P	P	P	G
Reduction in Volume	P	P	P	P	P	P	P	G
Implementability	G	G	G	G	G	G	G	G
Short Term Effectiveness	P	P	P	G	G	G	G	G
Long Term Effectiveness	P	P	P	P	P	P	P	G

P = POOR G = GOOD

TABLE 4
M-1 SETTLING BASINS
CHEMICAL FIXATION TREATABILITY TEST RESULTS

Method	Analyte	Before (mg/L)	Limits of Detection (mg/L)	After (mg/L)
EPA #7060	Arsenic	1,100	5	ND
EPA #7470	Mercury	610	0.2	56

The In situ vitrification alternative meets all of the assessment criteria based on an engineering scale treatability test including protection of human health and the environment and long term effectiveness. All of the organics are pyrolyzed (destroyed by heat) during the vitrification process and the mercury is volatilized for capture as part of the offgas system. The arsenic and other inorganic contaminants are immobilized by capture in the vitrified mass by either encapsulation or chemical bonding. The toxic chemicals either no longer exist or are not leached in human time scale from the vitrified mass.

CONCLUSIONS

Alternative 6, In-situ vitrification, was the preferred alternative. In general, a treatment alternative is preferable to a containment alternative at this site because the source volume is known, the waste characteristics are well-defined, there are high concentrations of contaminants, and because the source is actively contaminating groundwater. The advantages of in-situ vitrification are that the metals are either immobilized or recovered and that the organic contaminants are destroyed, thereby reducing the toxicity of the material.

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Ebasco Services, Inc. 1988. Final Phase I Data Presentation Report, Army Spill Sites, South Plants Manufacturing Complex, Task No. 24, Version 3.2. September 1988.

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SEARCH FOR A WHITE PHOSPHORUS MUNITIONS DISPOSAL SITE IN CHESAPEAKE BAY

INTRODUCTION

Several techniques were used during this investigation to determine the location of the WPMBA (see figure 1). A literature search was conducted to locate related information concerning the disposal, storage, and handling of white phosphorus. APG records, historical maps and aerial photos were reviewed. Manufacturers, former employees, and historians (National Archives, Library of Congress, U.S. Army Archives) were also contacted for relevant information. Finally, a geophysical investigation at the site was also conducted.

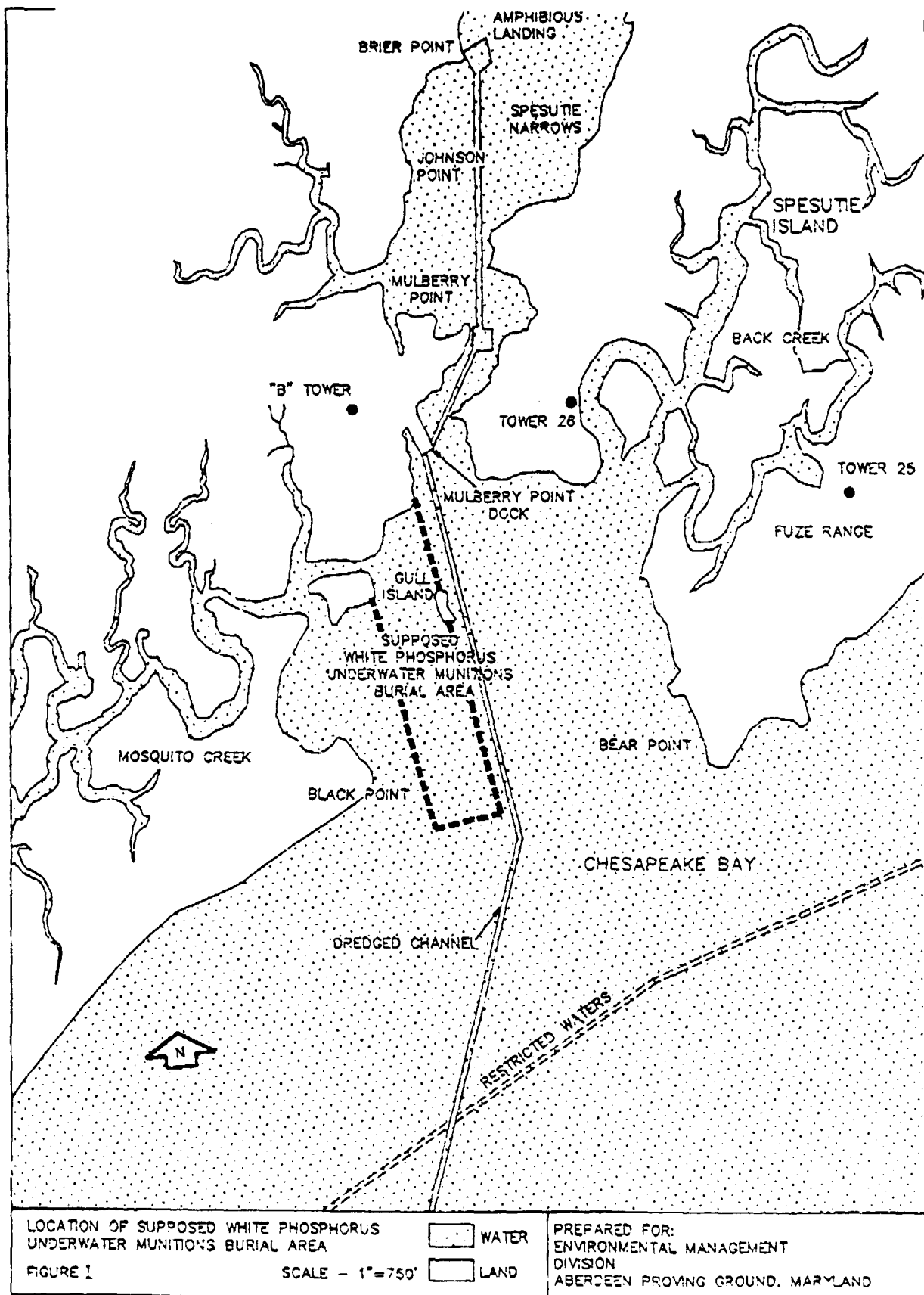
Based on the geophysical data, four areas were selected for sediment core analysis to determine if a burial site existed. A fifth area, the channel adjacent to the WPMBA, was selected for coring due to maintenance dredging concerns. A reference area was also selected north of the site in Spesutie Narrows. Due to the safety concerns in dealing with the burial area and the known presence of unexploded ordnance on APG, a remote coring operation was necessary.

A total of 60 cores were collected, ranging in depth from 1 to approximately 9 feet. Cores were screened on-site for high explosives and composite samples were collected for analysis. All samples were analyzed for elemental phosphorus, high explosives, and RCRA hazardous waste analyses. Select samples were analyzed for total organic carbon, grain size, and toxicity testing. Water samples were also collected at each of the areas cored and analyzed for elemental phosphorus and high explosives. Water quality measurements were recorded in each area and included temperature, pH, conductivity, salinity, oxidation-reduction potential, and dissolved oxygen.

Gull Island, which is located along the eastern border of the WPMBA, was examined as a potential disposal site. A geophysical survey was conducted to locate any potentially buried ferrous metals. Several test pits were excavated to examine the stratigraphy and soils of the island. Soil cores were collected from two locations and analyzed for elemental phosphorus, high explosives, and grain size.

The results of the investigation indicate that trace amounts of white phosphorus were detected in 11 of the 60 core samples at less than 5 ug/kg. No white phosphorus was detected in the water column, or on Gull Island. No high explosive compounds were detected in the water or sediment samples. RCRA analyses indicate that the sediment cores would not be considered a hazardous waste. Definitive boundaries could not be determined due to the diffuse and isolated nature of the contamination. No impacts upon the aquatic systems are expected. Release of white phosphorus is not expected unless the sediments are disturbed.





BAY

SITE BACKGROUND

The Aberdeen Area of APG was established in 1917 as the Ordnance Proving Ground. Testing of ammunition was begun in January of 1918. The open water area of APG totals approximately 37,000 acres. Large segments have been used as ordnance impact areas since 1917. There are an estimated four million unexploded and sixteen million inert projectiles of all calibers in these restricted waters.

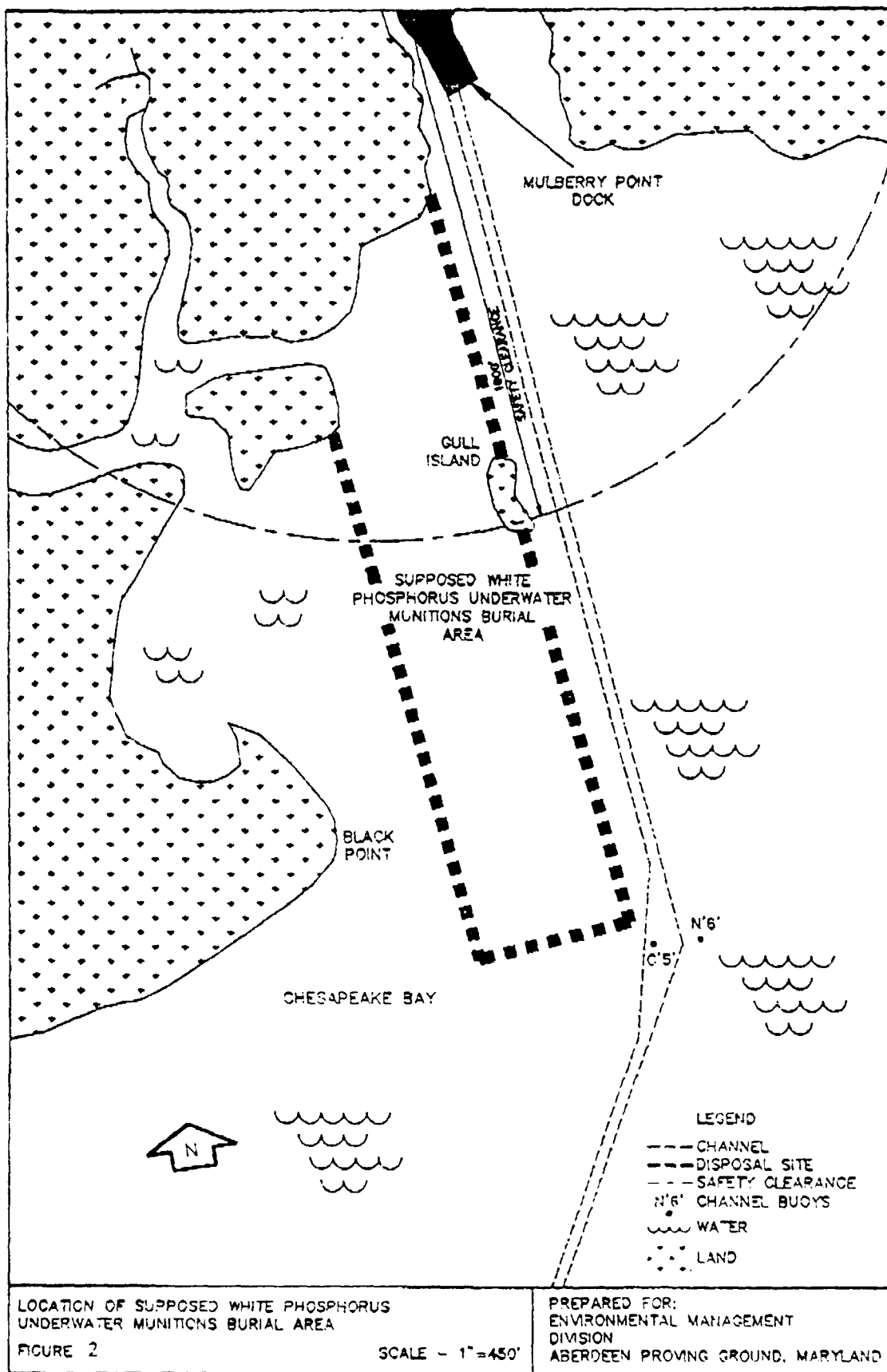
The WPMBA is located on the western side of the Upper Chesapeake Bay. The area (see figure 2) is situated in the shallow waters off the mouth of Mosquito Creek, between Black Point and Gull Island. Spesutie Narrows and Spesutie Island lie to the north and northeast respectively. The WPMBA is adjacent to and offshore of the Main Front Land Range Area which has been active since 1917. An estimated one million rounds of all calibers up to 16 inches have been fired at this range. The types of rounds fired included high explosives, anti-personnel, armor defeating, incendiary, smoke, and illuminating. Although the WPMBA is adjacent to this range, there are no records of the open water area of the WPMBA having been used as an impact area.

Based on interviews of former employees who worked on the base following World War I the existence of the WPMBA was discovered in the late 1970's. Reportly, an unknown amount of World War I white phosphorus (WP) munitions were buried in Chesapeake Bay in area of Black Point during the period 1920-1925. The ordnance supposedly consisted of United States, British, and French land mines, grenades, and artillery shells. Bulk phosphorus may also have been disposed. It is possible that this disposal event involved a single barge load of munitions; however it may have involved considerably more.

No evidence of a disposal site was observed in any historical aerial photographs reviewed. One major piece of information comes from Proclamation 2383, signed by President Franklin D. Roosevelt on January 24, 1940. Previously, two areas were designated a Migratory Waterfowl Closed Areas under a regulation adopted by the Acting Secretary of the Interior on December 12, 1939, under the authority of the Migratory Bird Act of July 3, 1918. One of the areas approved by the proclamation was entitled the "Phosphorus Area Unit". This proclamation was the only written document found that specifically mentions phosphorous and delineated the boundary of the area. The size of this area encompasses approximately 130 acres. It is assumed that the area described incorporated the WPMBA.

INVESTIGATION SCOPE

The purposed of this investigation was to answer questions related to releases to groundwater under the burial site, to potential adverse affects to the environment, aquatic organisms, higher food chain organisms, and human health that could result



should there be a release from this unit, and to considerations of the extent to which any past or future dredging activities may contribute to releases from this unit.

The field investigations reinforced some of the prevalent notions as to the location and extent of the former WPMBA; however, the geophysical results showed only a minor distribution of magnetic objects and intrusive sediment core sampling in those target area revealed only sporadic occurrences of detectable levels of white phosphorus. Likewise, bioassay techniques did not elucidate any clear toxic effect on aquatic life. These results lead to a conclusion that any safety or environmental hazard which may have existed in the past due the WPMBA no longer exists. It is still possible, however, that unexploded ordnance or other safety hazards may exist within the study area.

SUMMARY OF SITE RISKS

It is known that white phosphorus is a powerful systemic poison. It is absorbed through the skin, by ingestion, and through the respiratory tract. The lethal dose (oral ingestion) in adult humans is about 1 mg/kg body weight, but as little as 0.2 mg/kg body weight may produce toxic symptoms. Skin contact produces severe and painful burns, with destruction of the underlying tissue. Inhalation of vapors has produced tracheobronchitis and liver enlargement.

Another concern is the impacts of contamination through the food chain. White phosphorus contamination in various fish tissues has been shown to be toxic or lethal if ingested. However, due to the reactivity of white phosphorous, the transfer of this element through the food chain would not be expected to last. In terms of long term food chain contamination, the potential from white phosphorus is considered nil.

Bioaccumulation to an upper level consumer, such as waterfowl, has been considered. Again toxicity data is minimal but the lethal dose has been cited a 3 mg/kg. Several factors suggest that bioaccumulation may be negligible. Waterfowl are using the WPMBA during a few months in the winter season. Therefore, exposure to the small quantities detected should be minimal. Additionally, waterfowl lipid content during the winter is elevated. This may serve to isolate any white phosphorous ingested and prevent manifestation of acute symptoms. Further, large birds rather than sensitive precocial young would be utilizing the food resource. For these reason, sub-lethal effects on waterfowl should be isolated or of a low probability.

Based on the location of the WPMBA (Chesapeake Bay), the dispersed nature of the trace levels of white phosphorous contamination releases to groundwater are minor. The depth to bedrock in this region is between 500 and 1000 feet, and slopes to the southeast. Due to the remote nature of the WPMBA and its location in an estuarine environment it is unlikely the site

poses a threat to groundwater.

The no effect level for white phosphorus in sediment lies below 2 ug/kg (wet weight). All white phosphorus wet weight concentrations were below 2 ug/kg for the investigation. This indicated that the sediment contains no effect concentration of white phosphorus. The lack of detectable quantities of white phosphorus in the water column indicates the stability of the white phosphorus in the sediments. However, it is possible that white phosphorous could be released to the water column during disruption of the substrate.

Periodic storms and shifts in winds and waves re the cause for changes in the geomorphometric processes observed by aerial photographs at the site. An examination of the wind rose at Aberdeen Proving Ground indicates that winds which may cause accretion occur approximately 16% of the time. The WPMBA is sheltered from winds approximately 26% of the time. Waves of sufficient height and energy are required to cause significant geomorphometric changes and only occur with high winds. Winds greater than 17 knots in the erosional or accreting directions only occurred about 1% of the time. This indicated that significant erosion or accretion would only occur during high winds and the occasional severe storm.

Based on current site risk no impacts upon the aquatic ecosystem are expected. Release of any remaining white phosphorous is not expected unless the sediments are disturbed. Further, the removal of the trace amounts of white phosphorous detected is not technologically feasible, due to the risk to the workers, community, and environment that would result from the use of current technology. The goals for further action are based on preventing disruption of the sediment for any future dredging operations and on conducting investigations after storm events to remove any uncovered white phosphorus.

DESCRIPTION OF A "NO ACTION" PREFERRED ALTERNATIVE

The purpose of this investigation was to answer questions related to conditions at the site and the potential for current or future threats to human health or the environment. The lack of detectable quantities of white phosphorus in the water column, combined with the relatively low concentrations of white phosphorous in the few number of sediment samples and the depth which they were found, indicates that white phosphorous is not being released into the water column. Based on the presence of white phosphorous in the sediments after such a long burial, it seems unlikely that large quantities are being released to the water. Any remaining white phosphorus which may still be present could be released to the environment if the sediment is disturbed. The removal of any remaining white phosphorous is currently not technologically feasible, due associated risk to the workers, community, and environment inherent in application of available technology. It has been proposed to conduct

discretionary sampling prior to any dredging activities in the area and to conduct discretionary sampling prior the water column following major storm events, to prevent and to identify release to the environment. A five year review will be performed to determine whether any technological improvements have occurred which would favorably influence the feasibility of removing residual white phosphorus without the present risks to workers, community, and environment.

CONCLUSIONS

The following conclusion are listed to summarize the findings of this investigation:

1. Numerous metallic objects were detected surrounding and within the boundaries of the WPMBA. These objects may be ordnance from the WPMBA or from nearby firing ranges, or from other disposal activities.
2. No definitive boundaries for the WPMBA could be determined.
3. No high explosives were detected in the sediment or waters.
4. RCRA analyses indicated that the sediment cores would not be considered a hazardous waste.
5. No white phosphorous was detected in the water column. Releases of WP are not expected unless the WPMBA is disturbed.
6. White phosphorus was detected in trace amounts (<5 ug/kg) in 11 of 60 cores.
7. White phosphorus was detected dispersed throughout the site. These areas were widely spread in the general WPMBA and no discernable contaminant pattern or trend was evident.



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**DEVELOPMENT OF PROCEDURES FOR CONDUCTING PRELIMINARY
ENVIRONMENTAL SURVEYS AND CLEARANCE AT PROPOSED
CONSTRUCTION SITES ON U.S. ARMY INSTALLATIONS**

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1.0 INTRODUCTION

1.1 BACKGROUND AND PURPOSE

Subsurface soil contamination resulting from past use or disposal of munitions and other hazardous materials can halt construction of military projects and place construction workers at risk. The U.S. Army Toxic and Hazardous Materials Agency, therefore, is developing standard procedures for categorizing planned construction sites based on their historical use and potential for containing residual contamination. These procedures provide a standardized methodology for investigating construction sites to confirm or deny the presence of hazardous materials, such as volatile synthetic hydrocarbons, buried containerized materials, unexploded ordnance (UXO), and chemical agents.

The purpose of the Construction Site Survey and Clearance Manual is to provide guidance to Major Commands (MACOMS) and Engineering and Construction Project Managers responsible for Military Construction, Army (MCA), minor MCA, Army Family Housing (AFH) construction projects, and all other construction projects on Army installations, regarding proper techniques for preconstruction site investigation and clearance procedures. The manual provides uniform procedures for investigating and clearing sites at Army installations of hazardous materials, such as, volatile organics, buried wastes, and UXO, prior to construction. Information contained in the manual will improve the safety of such projects and decrease the risk of injury to military, civilian, and contractor personnel involved in their construction.

The Construction Site Survey and Clearance Procedures Manual was prepared by Environmental Consulting & Technology, Inc. (ECT, Tampa, FL) under contract to the U.S. Army Toxic and Hazardous Materials Agency. Subcontractors on the preparation of the manual were Technos, Inc. (Miami, FL) and UXB International (Chantilly, VA). This paper summarizes the procedures and methods detailed in the manual.

1.2 CLASSIFICATION OF CATEGORY I, II, AND III SITES

Army Regulation (AR) 415-15 requires that all proposed construction sites be evaluated by the installation for potential site contamination and categorized as one of the following:

- **Category I.** This site is located in a traditional non-hazardous location, such as in an administrative, recreation, or housing area. The installation has no reason to suspect contamination.
- **Category II.** Current and former industrial sites or other hazard-producing activity sites will fit into this category. This site category consists of perceived clean locations, which, due to former industrial or other activities within or near the site, or due to the uncertain nature of a site's historical usage, have the potential for contamination. Surveys required for Category II sites are of a general nature to investigate the site for a wide range of potential contaminants.



- **Category III.** Sites located in areas known to be contaminated are included within this category. Contamination will vary; e.g., a known disposal site as identified in previous studies or unexploded ordnance (UXO) at former range. Contaminants of concern are known, so that specific techniques can be used to verify the presence or absence of such contaminants.

The procedures for construction site survey and clearance are organized in a step-wise manner. Figure 1.2-1 depicts the elements of site survey and clearance. As shown, the survey and clearance process involves a preliminary site assessment that includes records review and examination of aerial photographs and site surface inspection to determine former usage of the site and potential for contamination. Following this preliminary site review, the proposed construction site is then classified as a Category I, II, or III site.

1.2.1 CATEGORY I SITES

Once the preliminary assessment is completed and the site has been classified as Category I, II, or III, additional environmental survey and clearance steps are performed as indicated in Figure 1.2-1. For sites classified as Category I, the results of the preliminary site assessment are recorded on DD Form 1391 and in paragraph D9, Summary of Environmental Consequences, of the Detailed Justification, and the construction project proceeds as planned.

1.2.2 CATEGORY II SITES

Sites classified as Category II require that several non-intrusive environmental survey methods be performed. These methods are a geophysical survey and a soil gas sampling and analysis survey. The application of geophysical methods and soil gas sampling and analysis to Category II sites is dependent on site-specific characteristics such as geology, soil types, depth to groundwater, and on information regarding the types of suspected contamination. This geological and contaminant information is collected during the preliminary site assessment (records review) and is used to provide guidance for selection and design of the geophysical and soil gas survey methods. These environmental survey methods also are designed based on specific details of the proposed construction project. These details include size of construction project, location and depth of soil excavations (e.g., foundations, conduit and utility lines, and subsurface dewatering requirements). The results of the geophysical and soil gas environmental survey investigations are then recorded on DD Form 1391 and in Paragraph D9, Summary of Environmental Consequences, of the Detailed Justification.

Some Category II sites may exhibit contaminants and/or site geologic conditions such that geophysical and soil gas methods are not effective survey techniques. This would be the case for non-volatile contaminants, radiological contaminants, biological (infectious) contamination, and contaminated groundwater occurring at depths below the effective range of geophysical and soil gas methods. Table 1.2-1 summarizes various contamination scenarios where geophysical methods, soil gas methods, as well as other investigative techniques would be applicable to verify if a proposed construction site contains soil and

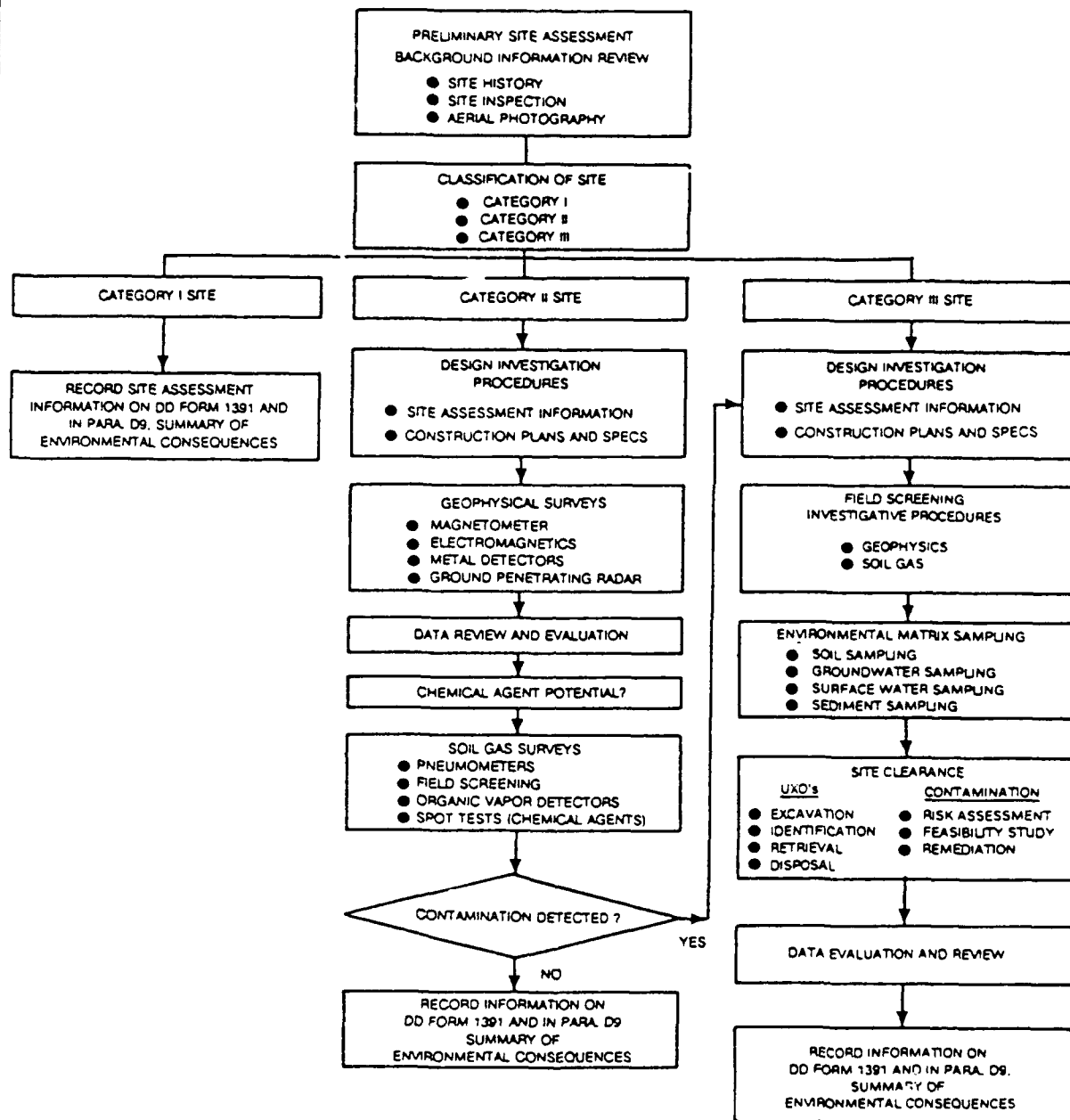


FIGURE 1.2-1
CONCEPTUAL ELEMENTS OF SITE INVESTIGATION
AND CLEARANCE

Source ECT, 1991

U.S. Army Toxic and Hazardous
Materials Agency.

Aberdeen Proving Ground, Maryland.



groundwater contamination. As shown in Table 1.2-1, geophysical methods and soil gas sampling are generally applicable to a wide range of potential contamination scenarios that could occur on or in the vicinity of a Category II site. In some situations, however, specific sampling and laboratory screening analysis of affected soil and groundwater is recommended. The decision to include this specific sampling in the site investigation would be made based on information collected from the preliminary site assessment (records review) and the details of the planned construction. Table 1.2-1 also includes a list of contacts for guidance in planning the site investigation methodologies.

1.2.3 CATEGORY III SITES

Sites that are known to be contaminated or contain possible UXO (e.g., former range areas) are classified as Category III sites. Survey and clearance procedures for these sites are conducted by specially-trained personnel using instrumentation and methodologies described in Section 5.0 of this manual. Sites that are known to have chemical agents or munitions that may contain chemical agents also are classified as Category III sites.

Sites classified as Category III will have specific known contaminants. The investigation and clearance procedures for these sites will need to be developed by the installation Environmental Office and Safety Office in coordination with the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA). Remediation/clearance of Category III sites will be conducted in compliance with applicable federal, state, and local laws and regulations. Investigation and clearance of such sites may require extensive field surveys, to include geophysics, soil sampling and analysis, groundwater sampling and analysis, and the associated requirements for coordination with federal and state environmental agencies. Completion of the preconstruction survey and remediation of a Category III site and its vicinity could encompass a number of years. Investigations will be site-specific and focused on contaminants of concern. As with Category II sites, the details of the particular construction project will serve to guide the design of the survey and clearance procedures.

2.0 PRELIMINARY ASSESSMENT

A preliminary site investigation is required for all proposed construction sites. The preliminary site investigation should be performed by the installation during the site selection process prior to initiation of design of a project.

The preliminary site investigation will involve the following tasks:

- Installation historical records review,
- Aerial photographic review,
- Site visual inspection, and
- Data review and evaluation.



Table 1.2-1. Summary of Investigative Techniques Applicable to Various Contamination Scenarios
(Page 1 of 2)

Potential Contamination	Recommended Survey Technique(s)	Guidance/Limitations/Comments	Point of Contact
Buried materials (drums, cans, containers, etc.)	1. Geophysics/soil gas	1. See sections 3.0 and 4.0	Note 1.
Landfills, debris dumps	1. Geophysics/soil gas	1. See sections 3.0 and 4.0	Note 1.
Burn pits; fire training areas	1. Geophysics/soil gas	1. See sections 3.0 and 4.0	Note 1.
Unexploded Ordnance (UXO's)	1. Geophysics	1. See sections 3.0 and 5.0	Note 2.
Volatile chemicals (fuels, solvents, etc.) spilled or disposed of on soil	1. Geophysics (EM)/soil gas	1. See sections 3.0 and 4.0	Note 1.
Volatile chemicals (fuels, solvents, etc.) in groundwater	1. Geophysics (EM)/soil gas 2. Groundwater sampling and analysis	1. Generally applicable to shallow groundwater depths (e.g., <20 ft). See sections 3.0 and 4.0. 2. If groundwater occurs at depths >20 ft and dewatering is anticipated during construction, a monitor well should be installed in the area proposed for dewatering and a groundwater sample collected and analyzed for contaminants of concern.	Note 1.
Non-volatile chemicals (metals, oils, grease, munition residues) spilled or disposed of on soil	1. Geophysics (EM) 2. Soil sampling and analysis	1. Geophysics (EM) applicable if contamination at high levels in soil. See section 3.0. 2. Soil samples should be collected from areas proposed for excavation. These soil samples should be analyzed for contaminants of concern.	Note 1.
Non-volatile chemicals (metals, oils, grease, munition residues) in groundwater	1. Geophysics (EM) 2. Groundwater sampling and analysis	1. Generally applicable to shallow groundwater depths (e.g., < 20 ft). See section 3.0. 2. Monitor wells should be installed in areas proposed for excavation or dewatering. Groundwater samples should be collected and analyzed for contaminants of concern.	Note 1.

Table 1.2-1. Summary of Investigative Techniques Applicable to Various Contamination Scenarios
(Page 2 of 2)

Potential Contamination	Recommended Survey Technique(s)	Guidance/Limitations/Comments	Point of Contact
Chemical agents in soil	1. Soil gas screening using field detector kit with laboratory confirmation	1. See sections 4.0 and 6.0.	Note 1.
Chemical agents in groundwater	1. Soil gas screening using field detector kit with laboratory confirmation 2. Groundwater sampling and analysis	1. Applicable to shallow groundwater depths (e.g., <20 ft). See sections 4.0 and 6.0. 2. If groundwater occurs at depths >20 ft, a monitor well should be installed and a groundwater sample collected and analyzed.	Note 1.
Asbestos-containing material (ACM) in soils	1. Soil sample collection with microscopic analysis	1. Code of Federal Regulations (CFR), Title 29.	Note 1.
Radiological contaminant wastes		1. Code of Federal Regulations (CFR), Title 10, Army Regulation (AR) No. 305-11.	Note 1.
Biological (infectious) wastes		1. 1990 OSHA Instruction CPL 2-2.44B	Note 1.

Source: Note 1. U.S. Army Toxic and Hazardous Materials Agency; Aberdeen Proving Ground, MD.
Telephone (301) 671-1511

Note 2. U.S. Army Engineer Division; Huntsville, AL.
Telephone (202) 504-4706

The primary objectives of the preliminary site investigation tasks are to:

- Develop an understanding of past activities and disposal practices at a site which may have resulted in site contamination,
- Identify possible contaminant receptors onsite or in adjacent areas, and
- Provide a preliminary identification of contaminant pathways.

Based on the records review and visual site inspection, the evaluator must determine whether there is any reason to suspect that contamination has potentially occurred through past installation activities in an area. If not, the site should be classified as Category I, and the gathered information should be entered in appropriate blocks on Form 1391. If there is any reason to suspect a site to contain contamination, it must be classified as a Category II or III site and investigated by the following required procedures.

3.0 GEOPHYSICAL PROGRAM

3.1 INTRODUCTION

A surface geophysical investigation of the proposed site and its vicinity is required for all Category II and Category III sites, if practical for the suspected contamination. Geophysics can be used for an assessment of natural hydrogeologic conditions, an assessment of contaminants within the natural system, and most importantly, for the detection of buried wastes or UXO.

3.1.1 BACKGROUND

The preliminary assessment procedures described in Section 2.0 will have been conducted prior to planning the geophysical field procedures. Review of the historical documents and a reconnaissance of the site surface will aid in the proper placement of geophysical field survey grids.

A site map of noted disturbed areas is used to assist in the design of the geophysical surveys. In addition, the details of the proposed construction, such as areas of building locations; depths and locations of excavations for foundations, utilities, and conduits; and parking areas, must also be addressed in planning the geophysical surveys.

Geophysical investigations are useful as a general survey technique for site screening. However, there may be some specific cases where geophysical methodologies are not effective due to the type of contamination and/or the manner in which the release of suspected contamination occurred.



3.1.2 THEORY OF APPLICATION

Geophysical methods use certain principles of physics to explore and investigate subsurface conditions. These principles include the propagation of electromagnetic (EM) waves, electromagnetic induction, and use of the earth's magnetic field. These methods provide insight into subsurface conditions in some cases much like a x-ray provides a "picture-like" section of the human body. The primary applications for the geophysical methods as employed in this document are:

- Locating and mapping buried waste and disposal trenches;
- Locating and mapping man-made structures such as utility pipes and cables, drums, tanks and buried foundations; and
- Locating UXO.

These methods can also be used to characterize natural soil and rock, characterize hydrogeologic conditions, and to map contaminant plumes. However, the purpose of this document is directed towards the use of geophysical methods for the three objectives listed above.

There are four geophysical methods commonly used for such site investigations:

- Ground Penetrating Radar (GPR);
- Electromagnetic (EM);
- Magnetometer (MAG); and
- Metal Detector (MD).

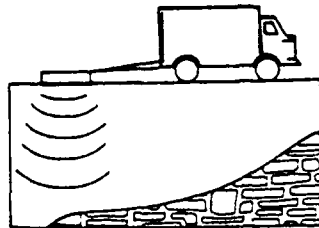
While additional geophysical methods are currently available and others are being developed, the manual addresses these four methods because of their wide range of application. Figures 3.1-1 and 3.1-2 conceptually illustrate the physical principles of GPR, EM, MAG, and MD.

These methods do not require intimate ground contact and provide a rapid means of obtaining subsurface information. While EM and MAG may be used to gather data on a station-by-station basis, a common aspect of each of these four methods is the ability to provide continuous data acquisition along a survey line. While station measurements using EM and MAG are adequate to locate large targets such as sizeable burial trenches, continuous data acquisition (high-resolution data), is critical for successful detection and location of smaller objects (targets) such as a single steel drum or UXOs (i.e., hand grenades or shells). In many cases, data is obtained in real-time and requires little or no processing. Results can often be interpreted directly in the field. Caution, however, should be used if relying on the initial interpretation without analysis and benefit of other necessary data.

Geophysical methods, like any other means of investigation, have advantages and limitations. There is no single, universally applicable geophysical method and some methods are quite site-specific in their performance. Thus, the user must understand the advantages and limitations of each method and carefully select the method or methods and how they are applied to specific site conditions to meet project requirements. The success of a geophysical method depends primarily upon the following three factors:



GPR - A reflection method that uses high frequency electromagnetic waves reflected from subsurface targets to provide a "picture-like" profile of subsurface conditions.



EM - A method that measures the conductivity of soils and rocks by inducing relatively low frequency electromagnetic currents. The method is also used to locate buried materials with a high specific conductance or buried metal (both ferrous and non-ferrous).

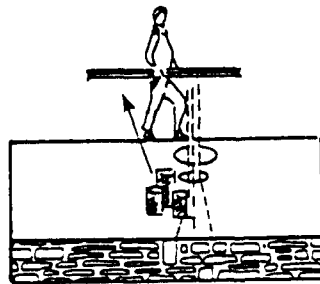


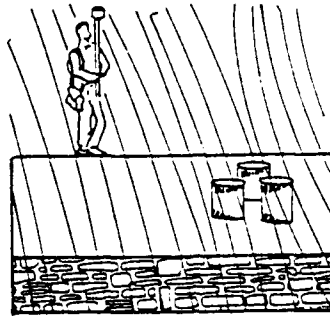
FIGURE 3.1-1
PRINCIPLES OF GROUND-PENETRATING RADAR
(GPR) AND ELECTROMAGNETICS (EM)

U.S. Army Toxic and Hazardous
Materials Agency

Aberdeen Proving Ground, Maryland



MAG - A method that measures the intensity of the earth's magnetic field. The method is used to locate buried metal by measuring the local distortions of the earth's field caused by the buried metal. The method can only be used to locate ferrous metals.



MD - A method to locate buried metals by inducing relatively low frequency electromagnetic currents within the buried metal. The method can be used to locate ferrous and nonferrous metals.

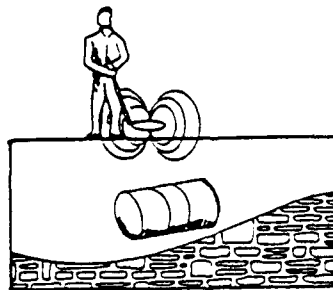


FIGURE 3.1-2
PRINCIPLES OF MAGNETOMETER (MAG) AND
METAL DETECTION (MD)

U.S. Army Toxic and Hazardous
Materials Agency

Aberdeen Proving Ground, Maryland

1. The existence of a sufficient contrast between the measured properties of the target and background conditions. If there is no measurable contrast, the target will not be detected.
2. The size of the target; if the size of the target is sufficiently small it will not be detected.
3. The depth of the target; as the target becomes deeper, there will be a point where it can no longer be detected.

The Site Survey and Clearance Procedures Manual provides a brief description of each of the four geophysical methods, along with the advantages and limitations of each method.

4.0 SOIL GAS PROGRAM

4.1 INTRODUCTION

A soil gas sampling program is required for Category II and Category III sites if the existing documentation and/or data substantiates a need for investigation of volatile organics or military chemical agent compounds. For Category II sites, the soil gas program is conducted following the completion of the geophysical investigation. Soil gas sampling is used to detect volatile organic vapors which may be present in the pore spaces of near surface or vadose zone soils, and which may be released during construction excavation. The soil gas vapors or skin contact with contaminated soils could be harmful to the health of construction personnel.

Soil gas surveys are useful as a general survey technique for site screening. There may, however, be some specific cases where soil gas sampling is not effective due to the type of contamination (e.g., non-volatile compounds) and/or the manner in which the release of suspected contamination occurred.

4.1.1 DESCRIPTION

A soil gas contaminant investigation refers to a method for investigating underground contamination from volatile chemicals such as industrial solvents, cleaning fluids, and petroleum products by looking for traces of their vapors in the shallow soil gas. The method also is applicable to military-specific chemicals such as chemical agents. The method involves pumping a small amount of soil gas out of the ground through a hollow probe driven into the ground and analyzing the gas for the presence of volatile contaminants. The presence of contaminants in the soil gas usually means that there is contamination from the observed compound either in the soil zone near the probe or in contaminated groundwater below the probe.

Figure 4.1-1 is a conceptual representation of contaminants volatilizing from soils at a buried waste or spill site. As shown, contaminants also can migrate due to leaching through the unsaturated zone and into the underlying water table. As the contaminant plume migrates in the direction of groundwater flow, volatilization also occurs into the overlying soil gas.



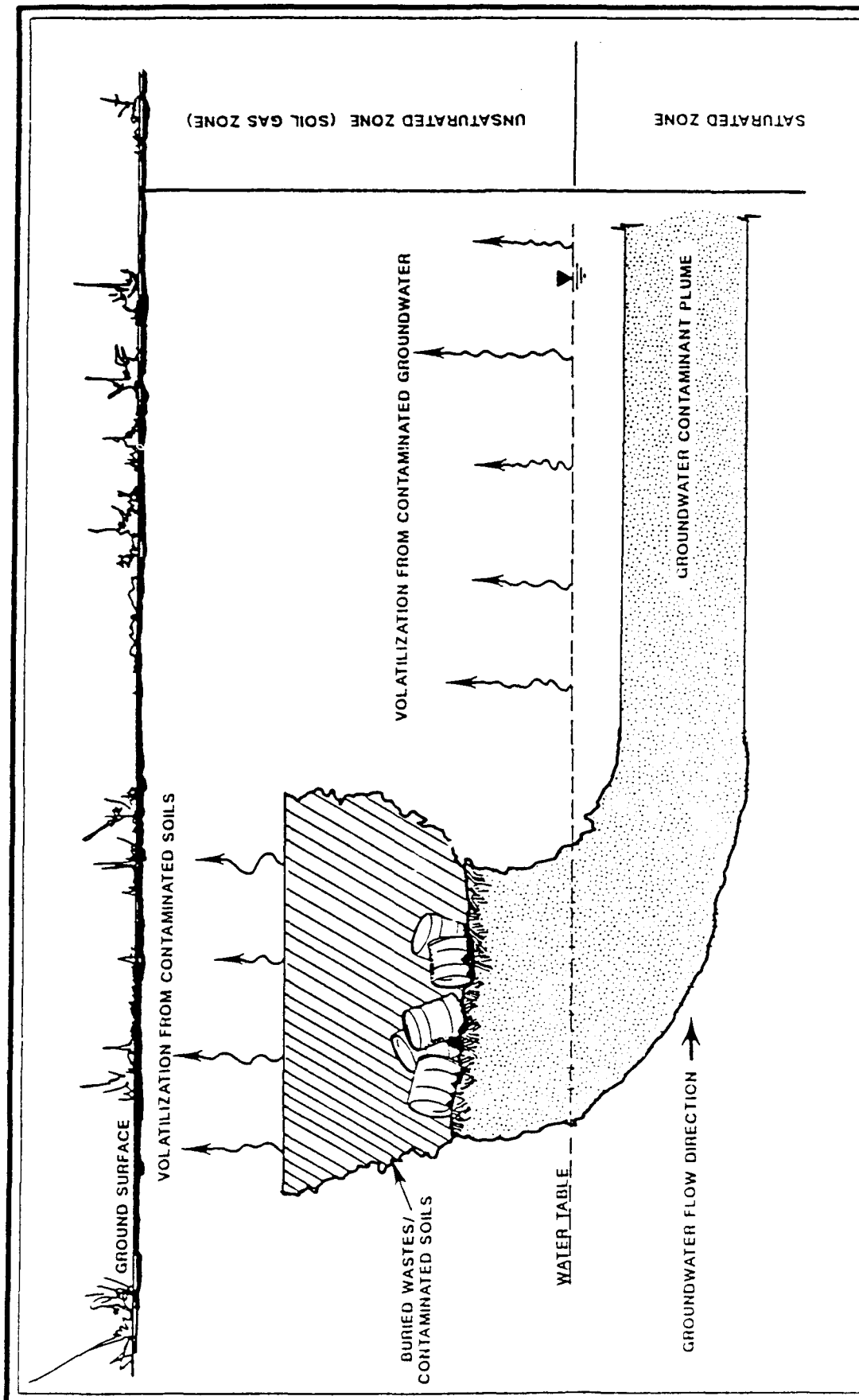


FIGURE 4.1-1
CONCEPTUAL REPRESENTATION OF CONTAMINANT VOLATILIZATION
FROM SOILS AND FROM CONTAMINATED GROUNDWATER

Source: ECT, 1991

U.S. Army Toxic and Hazardous
Materials Agency

Aberdeen Proving Ground, Maryland

The sampling and analysis of this soil gas is a rapid and useful method for screening for indications of subsurface contamination in soils or groundwater.

The soil gas analysis is generally performed in the field so that samples do not have to be packed or shipped. The analytical results, therefore, are available immediately and can be used to help direct the investigation. The soil gas survey investigation is conducted by analyzing soil gas samples in areas of the site proposed for excavation during construction or which exhibit anomalous geophysical measurements.

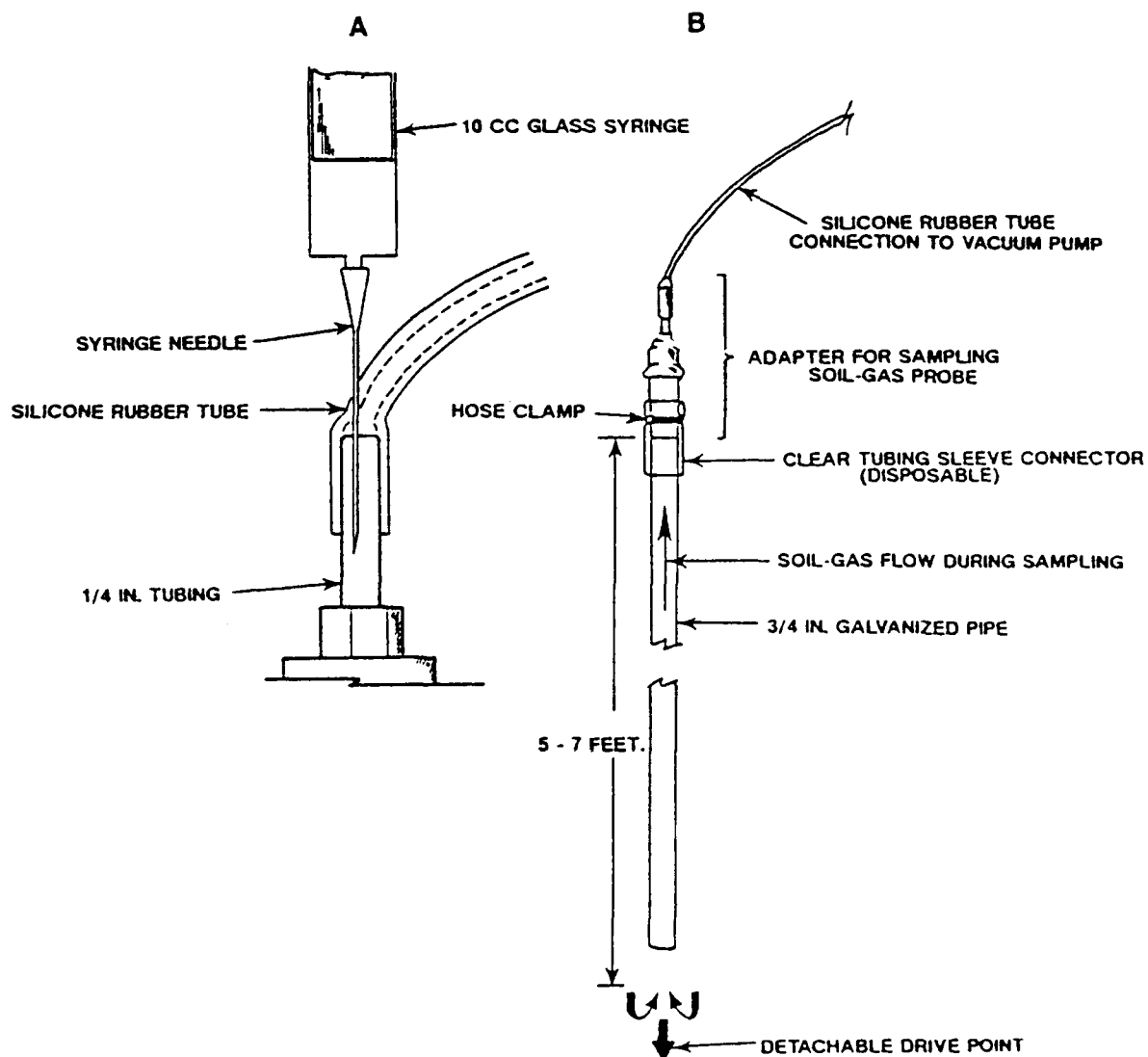
Soil gas surveys have the potential for providing a good deal of useful information. Most petroleum-related wastes contain volatile aromatic hydrocarbons such as benzene, toluene, xylene, ethyl benzene, and semi-volatiles such as naphthalene. All common industrial cleaning or degreasing solvents are volatile. These solvents include, but are not limited to, trichloroethene, tetrachloroethene, carbon tetrachloride, trichloroethane, trichlorotrifluoroethane (freon), and methylene chloride. Pesticide compounds and military-specific chemical agents also exhibit some degree of volatility that allows the detection of these chemicals in soil gas samples.

There are several soil gas sampling and analytical techniques and they should be chosen carefully for a given site condition. For the purposes of the Site Survey and Clearance Procedures Manual, a soil gas survey is defined as a technique which uses some device to make a shallow (up to 20 ft) hole and collect a gas sample directly from the soil at the point of deepest penetration. Steel tubes or pneumometers are generally used for soil gas collection and monitoring. Analyses generally are made in the field with a portable organic vapor analyzer (HNU or OVA) or a portable gas chromatograph, or in the laboratory for samples collected in sample Tedlar bags. Figures 4.1-2 and 4.1-3 illustrate soil gas sampling techniques.

The standard method of testing for military chemical agents is to take air samples with the U.S. Army ABC-M18A2 Chemical Agent Detector Kit. This small kit consists of detector paper, used if suspected agents are found in liquid form, and an aspirator bulb which is used to take vapor (e.g., soil gas) samples with testing tubes and fiber discs. The use of the aspirator bulb for testing soil gas vapors is illustrated in Figure 4.1-4. All of these tests are completely conducted onsite and the results are immediate. The kit is capable of testing for all common U.S. manufactured chemical agents and is also equipped with a non-reactive tube containing an absorbent material for obtaining samples of unknown vapors for subsequent laboratory analysis. All positive "tests" for chemical agents must be confirmed by laboratory analysis.

Another method of detecting and monitoring chemical agents is the Chemical Agent Monitor (CAM). CAM is a recently developed portable, hand-held instrument used to monitor the presence of nerve and blister agents. The level of toxic hazard is assessed by an on-board microcomputer and indicated by an LCD.





A. CLOSE UP SYRINGE SOIL GAS SAMPLING THROUGH EVACUATION LINE.

B. DIAGRAM OF SOIL GAS SAMPLING PROBE WITH ADAPTER FOR SAMPLING AND EVACUATION OF THE PROBE AFTER IT IS DRIVEN INTO THE GROUND.

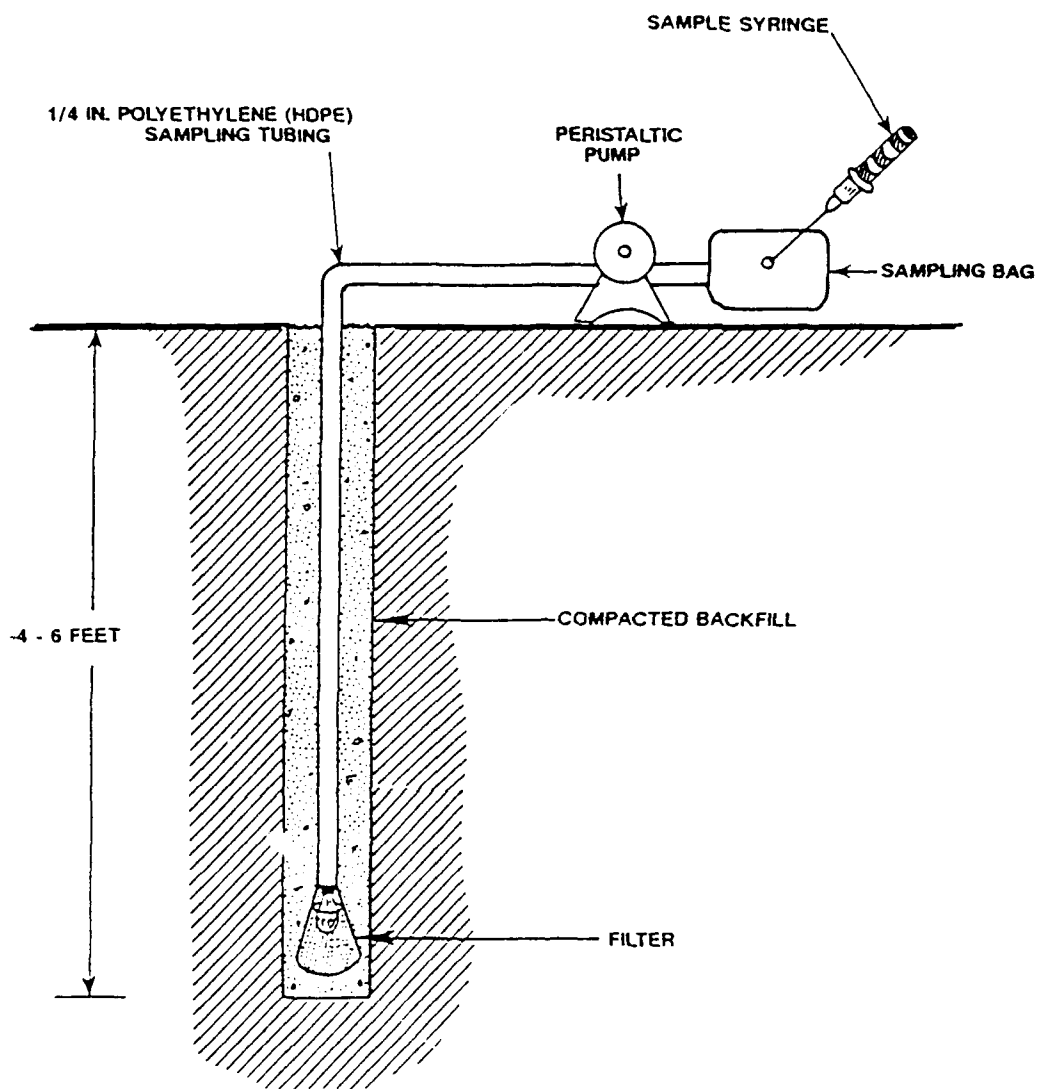
FIGURE 4.1-2
SOIL GAS MONITORING STATION SHOWING THE
TECHNIQUE OF IN-LINE SOIL GAS SAMPLING

Source: TRC, 1984

**U.S. Army Toxic and Hazardous
Materials Agency**

Aberdeen Proving Ground, Maryland





NOT TO SCALE

FIGURE 4.1-3
SOIL GAS MONITORING STATION SHOWING SOIL
GAS COLLECTION INTO TEDLAR SAMPLING BAG

Source: KARABLY AND BABCOCK, 1989

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Aberdeen Proving Ground, Maryland



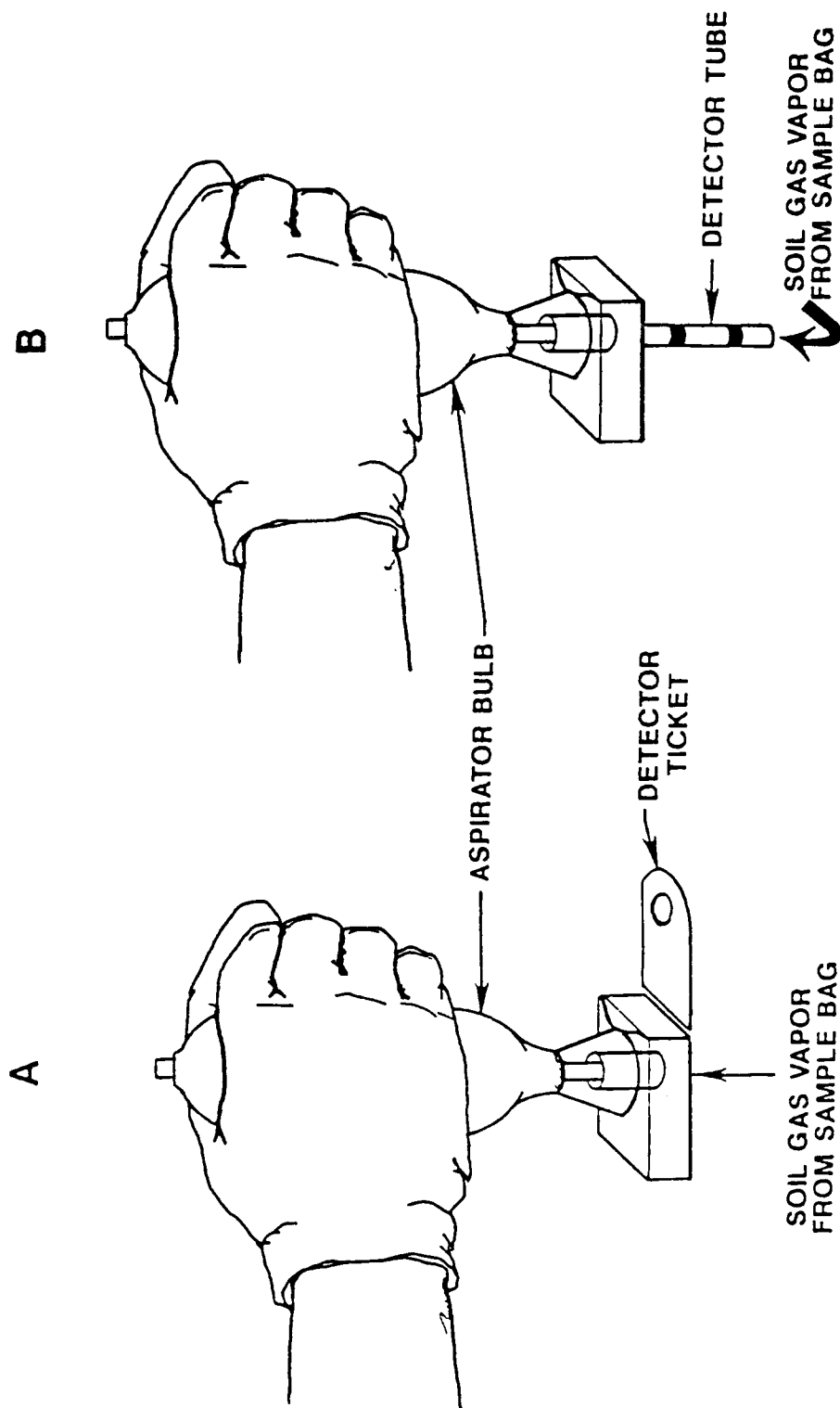


FIGURE 4.1-4
ILLUSTRATION DEMONSTRATING USE OF ASPIRATOR FOR TESTING
VAPORS USING THE M18A2 CHEMICAL AGENT DETECTOR KIT

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Historically, Chemical Warfare School training utilized glass vials containing dilute chemical agents mixed with a volatile carrier (e.g., carbon tetrachloride). Therefore, positive indications of agent compounds may also be associated with halogenated solvent detection.

Chemical agent testing should only be performed by military-trained EOD personnel or experienced civilian contractor personnel qualified to conduct this type of testing. All work involving chemical agent testing on U.S. Army installations must be in accordance with AR 50-6, "Chemical Surety", which contains responsibilities, procedures, chemical accident/incident notification, and safety requirements.

5.0 UXO DETECTION AND EXCAVATION PROCEDURES

5.1 INTRODUCTION

If historical research of a prospective construction site indicates the possibility of the presence of UXO, the site must be classified as a Category III site. Even though the site is classified as Category III, it may still be a feasible construction site either because of the nature of UXO contamination (e.g., inert) or the capability to "clear" the construction site.

If, for example, the area is known to have been a former artillery range, UXO contamination will almost certainly be found during the initial site survey. But this type of contamination is relatively easy to detect and remediation is possible using military Explosive Ordnance Disposal (EOD) units or civilian UXO contractors.

On the other hand, an area suspected to contain an old ordnance dumping or burning site may present the further complications of soil and groundwater contamination or deeply buried concentrations of unstable ordnance items. It may, however, still be economically feasible to proceed with construction after the initial survey is conducted.

The information in the following sections analyzes further the characteristics of common ordnance items and describes the basic methods used by military trained Explosive Ordnance Disposal personnel. The U.S. Army Engineer Division, Huntsville, is a source of expertise and assistance in the investigation/clearance of potential UXO sites.

The plans and specifications of the proposed construction project need to be reviewed as part of the UXO survey planning. These construction details will determine the areas and the necessary depth(s) to be surveyed. All areas proposed for excavation must be specifically surveyed for UXO if the potential exists for the presence of these items.

5.2 SURFACE SEARCH

The surface search is primarily a visual search often assisted by magnetometers. A surface search would be a valid search method in the case of an artillery range or an area previously



used for bulk disposal of ordnance by detonation. In both of these cases, dud rounds or items not completely destroyed in a bulk disposal by detonation (kick-outs) can be expected to be found lying on the surface of the search area.

In the case of a large artillery range, a large search crew of up to 20 people can safely be used. Only three or four EOD trained personnel are required to safely conduct this search. The search crew must be trained in what to look for and how to best identify ordnance items. They then form a straight line and guide on one individual leading the search, and maintain a distance to each other that is close enough to allow adjacent searchers to visually overlap each other's search area. The line of searchers proceeds along at a slow pace and uses red marker flags to mark suspected ordnance items. The searchers must not touch a suspected item because they are not EOD trained. The three or four EOD technicians walk behind the search line and inspect every marked item to identify if it is in fact hazardous UXO. If it is, they will leave the marker flag in place and return later to dispose of the item.

This method is safe, quick and efficient to use in areas on most artillery and bombing ranges where there is very little vegetation. If vegetation, such as knee-high grass, exists, the search is complicated due to the lack of visibility. Grass should be burned off so the survey can be safely conducted. In this case, the use of inexpensive "treasure finder" type metal detectors can greatly increase the safety and efficiency of the search. Due to the increased danger and more technical nature of this surface search, only EOD trained personnel should be allowed to participate. Again, the searchers, armed with metal detectors will walk in a line marking any ordnance items found for disposal later.

The following discussions of search methods for shallow-depth UXO, medium-depth UXO, and deep-depth UXO are provided only as general information. These UXO depths may not be as easily categorized in practice.

5.3 SEARCHING FOR SHALLOW BURIED UXO

The search for shallow buried UXO similar to the surface search described above, but it is complicated by the fact that the ordnance may be covered with 1 to 18 inches of earth. This is a reasonable assumption for a minefield or heavy artillery range where dud projectiles are large enough to penetrate the earth. In this case, only EOD-trained personnel will be allowed to sweep the area because of the high degree of proficiency and experience required. They will follow an organized search pattern and use higher quality ordnance detectors, such as the Foerster unit. This search will proceed at a slower pace than the surface search because of the need to excavate all contacts. Again, all hazardous UXO will be marked for disposal later.

In the case of some new land mines, the ordnance is designed and constructed with non-metallic components intentionally to be undetectable by conventional ordnance detectors. Although the possibility of encountering a minefield of this type on a construction project is small, the construction project leader should be aware of the fact that technology exists to detect non-metallic mines using sophisticated x-ray techniques and by detecting the

interaction of radioactive material with the explosive filler in the mine. These methods, and others under development, are extremely sophisticated and are constantly evolving.

5.4 SEARCHING FOR MEDIUM DEPTH UXO

A medium depth search would be indicated in the case where ordnance is suspected to have been buried in shallow trenches. In this case a locator, like the Foerster, could be used to determine the location of burial trenches which would then require careful hand excavation to positively identify. Large artillery may, in some cases, penetrate this deep and would be handled in the same way as the shallow search. Of course, the deeper the UXO and the denser the concentrations found, the more time consuming the search will become.

5.5 SEARCHING FOR DEEP DEPTH UXO

Only dud bombs, large artillery projectiles, or UXO disposed of by burying in a deep pit should be located deeply underground. In the case of dud bombs, their presence will be indicated by the presence of an entry hole unless the firing was years previously. EOD technicians are trained in the proper methods of excavation of dud bombs which can be speeded up by the use of a backhoe in some cases.

UXO buried this deeply as a method of disposal will probably be present in large quantities and should, therefore, have left an easy to follow historical trail to point to its existence. More sophisticated geophysical survey methods would be indicated in this case, followed by hand or remotely operated equipment excavation to gain access to the UXO for proper identification.

5.6 IDENTIFICATION OF UXO

The purpose of performing excavation is to gain access to the UXO in order to identify it. Once access is achieved, the EOD technician will use EOD publications and personal experience to positively identify the UXO. They, then, will be able to formulate a safe procedure for the disposition of the item. Such characteristics as type, size, fuze used, color, material of construction, etc. will be used to identify the item. If a positive identification is not possible due to deterioration of the UXO, EOD personnel may choose not to move it and have it detonated in place.

5.7 UXO DISPOSAL PROCEDURES

The method of disposal chosen by the EOD technician will depend upon the identification of the UXO and its location.

5.7.1 DETONATION IN PLACE

Commonly referred to as a "BIP" (Blow In Place), this method is the safest and most efficient method of disposal for small quantities of dangerous UXO. If the location of the UXO can withstand a high order detonation of the UXO, the EOD technician will place a



small quantity of high explosive on the UXO, in a manner prescribed by the applicable technical publication, and initiate the explosive. After this procedure, the site should be checked by the EOD Technician to ensure complete destruction of the UXO.

5.7.2 REMOVAL AND OFF-SITE DISPOSAL

This method of disposal will be applicable in the following cases:

1. Disposal of a large quantity of UXO items that can safely be transported to another location for mass disposal, and
2. The location of the UXO cannot withstand a high order detonation.

In the above cases, the UXO will be carefully collected, transported and disposed of in one or more large disposal shots. If the item is determined to be hazardous but cannot be disposed of onsite, the EOD technician will first perform a render safe procedure (RSP) on the UXO. The procedure, outlined in the applicable EOD publication, will be performed remotely for maximum safety and, if successful, allow the item to be safely transported for disposal by detonation or open burning at another approved location.

6.0 CHEMICAL AGENT DETECTION AND OPERATING PROCEDURES

6.1 INTRODUCTION

Operating in an environment that is contaminated with chemical agents is a very complex process that requires trained personnel and specialized equipment. The logistics required for sustained operations in toxic environments can be staggering and only properly trained personnel can perform under the adverse conditions presented by this situation. For the purpose of a site survey that is designed only to confirm or eliminate the possibility of chemical agent contamination, a smaller effort is reasonable. All operations involving chemical agent detection and identification must be in accordance with AR 50-6, "Chemical Surety".

Just as in an ordnance survey, historical research can establish the type of threat present by establishing which agent or agents are most likely to be present. The following basic qualities of chemical agents determine the main threats to personnel when performing site investigations where chemical agents may be present.

1. Persistent agent--An oily based compound that tends to evaporate slowly and therefore remain a hazard longer in the immediate area.
2. Non-persistent--A volatile-based agent that tends to evaporate quickly and disburse quickly over a large downwind area, but decreases in intensity rapidly.

All work involving chemical agent testing on U.S. Army installations must be in accordance with AR 50-6, "Chemical Surety", which contains responsibilities, procedures, chemical accident/incident notification and safety requirements. However, the possibility exists of



encountering chemical agents during any excavation or drilling operation and the following information is, therefore, included to inform the users of this publication of recognized detection procedures and appropriate responses to the detection of toxic chemical agents on a construction site.

6.2 FIELD SCREENING

Field screening requires that specially-equipped EOD personnel or experienced civilian contractor personnel enter the area and perform tests to determine if toxic agents are present. The EOD unit or contractor will first establish a command post situated up-wind from the suspected contaminated site. Before entry of the investigation team can take place, a hotline and contamination reduction zone will be established to prevent the spread of contamination outside of the suspected contaminated area. Equipment for rapidly decontaminating investigation party personnel will be set up in the contamination reduction zone and medical personnel will be onsite in case an emergency occurs. An evacuation plan for rapid decontamination and transportation of injured or contaminated personnel to the nearest hospital should also be established.

The investigation party will always work in pairs with one member acting as a safety observer, attempting to avoid all contamination and observing the other member of the team for signs of exposure. Everyone that crosses the designated hot line must be wearing the proper level of protective clothing, as determined by the EOD Team Leader.

The standard method of testing is to take periodic air samples with the U.S. Army ABC-M18A2 Chemical Agent Detector Kit. This small kit consists of detector paper, used if suspected agents are found in liquid form, and an aspirator bulb which is used to take vapor samples with testing tubes and fiber discs. All of these tests are completely conducted onsite and the results are almost immediate and accurate. The kit is capable of testing for all common U.S. manufactured chemical agents and is also equipped with a non-reactive tube for obtaining samples of unknown vapors for subsequent laboratory analysis.

The investigation party will cross the hot line and install soil gas sampling probes on a grid pattern. Soil gas vapor samples will then be collected from each of the soil gas sampling probes. If no contamination is initially detected, they will continue to survey with the M-18 Detector Kit until a source of contamination is found or the area is determined to be free of obvious chemical contamination. If contamination is detected, the investigation team should take samples with the inert "white tubes" supplied with the M-18 Kit and they should be sent to a laboratory for confirmatory analysis.

Following either a positive or negative site investigation for toxic chemical agents, the inert "white tubes" should be used to sample the most likely source of the suspected contamination. These can then be sent to a laboratory for further analysis to insure that toxic agents are not present. All positive "tests" using the M-18 screening kit must be confirmed by laboratory analysis.



6.3 OPERATING PROCEDURES FOR POSITIVE INDICATIONS OF CHEMICAL AGENTS

At the first indication of the presence of toxic chemical agents, the person in charge of the site must take the following steps to protect personnel:

1. Inform local authorities (base police, commanding Officer, nearby civilian authorities);
2. Evacuate all personnel from the down-wind side of the suspected hazard in accordance with local directives;
3. Request the assistance of the local EOD unit or a UXO civilian contractor to investigate the site and determine the extent of the hazard.
4. Perform subsequent actions, including contracting, in accordance with AR 50-6 "Chemical Surety".

Under no circumstances should personnel not specifically trained in operations in a toxic chemical environment be allowed to enter the area.

It is entirely feasible to completely remediate a chemically contaminated site economically. But, when positive indications of contamination by toxic chemical agents exist, remediation efforts are conducted by trained personnel.





RAPID SCREENING OF SUSPECTED HAZARDOUS WASTE-CONTAMINATED STRUCTURES
USING A MOBILE MASS SPECTROMETER

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Michael S. Ford and Steve Freudenberger, Science and Technology Corporation
under contract to
U.S. Army Chemical Research, Development and Engineering Center

ABSTRACT

Structures which have been contaminated with hazardous chemicals pose a threat to public health and the environment. Demolition of such structures and disposal of the rubble can be dangerous and costly without first sampling the building materials for the existence of the hazardous chemicals. Such sampling can be costly and time-consuming using existing methods. The German Army has developed a mobile mass spectrometer for use as a battlefield chemical agent detector. This detector, an electron-impact type quadrupole mass spectrometer, can be programmed by the operator to simultaneously detect all types of volatile industrial chemicals as well as chemical warfare agents. It therefore shows much promise as a sampling device which can provide real-time data concerning the existence of suspected hazardous chemicals on building surfaces. Methods for the use of this instrument and some of the field results obtained with this device at a military installation are described.



RAPID SCREENING OF SUSPECTED HAZARDOUS WASTE-CONTAMINATED STRUCTURES USING A MOBILE MASS SPECTROMETER

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Michael S. Ford and Steve Freudenberger, Science and Technology Corporation
under contract to
U.S. Army Chemical Research, Development and Engineering Center

June 14, 1991

I. Introduction.

There exists a major problem within the military and industrial infrastructure in the U.S. concerning buildings that have been used to house dangerous substances and chemical operations. Structures which have been contaminated with hazardous chemicals can pose a threat to public health and the environment. The demolition of these buildings and the restoration of the area which they occupy is a major concern. Often, the histories of such structures is unknown or unclear; no one remembers what chemicals were used in the building and no good records exist. The problem is the potential cost of conducting such a demolition operation. The structure must be sampled before, during, and after demolition to insure that no residual chemicals are present which may endanger demolition workers or contaminate the landfill to which the rubble is sent. The need to send large amounts of rubble to a hazardous waste landfill could send the cost of a demolition project soaring. Sampling of the structure and its building materials can identify the contaminated parts, but such sampling is time-consuming and costly, and can delay the demolition procedure for weeks, if not months. The problem is widespread, but for the purposes of this paper the situation of Building E5625 at Aberdeen Proving Ground, Maryland will be studied (Reference A). This building was used for years as a pilot plant for a number of chemical operations involving chemical warfare agents and the chemicals used to make and detoxify them. A wide variety of chemicals was used in the building, and the Army would now like to demolish the building and remove the rubble.

II. Statement of Problem.

Though the demolition of such buildings involves a wide variety of problems, the sampling operation described above is the focus of this paper. Traditional sampling requires that material be removed from the site and taken to a laboratory for analysis. Field crews often don't know if the location they are sampling is contaminated or not, meaning they must operate in protective clothing. Many samples must be taken to insure that no potential contamination is missed; most of these samples are often from clean areas, producing little useful data while still costing the same to analyze as the contaminated samples. At hundreds to thousands of dollars per sample (including costs of the sampling crew as well as laboratory costs), costs can quickly escalate. Analytical times of days (for individual samples) to weeks or months (for numerous samples) are not uncommon. What is needed for such an operation is a real-time chemical sampler which can quickly and accurately identify contaminated areas in structures, allowing cleanup crews to know immediately where the contamination is and to implement their sampling and demolition procedures accordingly.



III. Description of Equipment.

A. Introduction. The German Army has developed a mass spectrometer for use as a battlefield chemical agent detector, which has been tested extensively and adopted by the U.S. Army (Reference B). This detector, the MM-1 Mobile Mass Spectrometer, manufactured by Bruker-Franzen Analytik GmbH of Bremen, Germany, is a portable mass spectrometer. It can be programmed by the operator to simultaneously detect all types of volatile industrial chemicals as well as chemical warfare agents.

B. Hardware Description. The MM-1 is a quadrupole electron impact mass spectrometer with a specialized sample inlet system designed primarily for detection of liquid chemical warfare agent droplets on a battlefield. The sample inlet system consists of a silicone rubber membrane attached to a 3 meter capillary line, with heaters on both the membrane holder and the capillary line. Droplets are contacted by the membrane and are immediately volatilized and conducted through it (if soluble in the silicone rubber; water and other insoluble substances mostly remain outside the membrane). Once through the membrane, the vapors pass into the capillary line by means of a pump pulling ambient air across the back of the membrane and through the capillary as a carrier gas. The capillary transports the vapors to the mass spectrometer inlet, where a second membrane transmits the substance to the ionizing area while maintaining the high vacuum needed in the mass spectrometer. The substance is then bombarded with electrons, fragmented into smaller ions, and the ions are detected with regard to mass number and quantity (abundance). Each compound has a unique spectrum of such fragments, so the computer can compare the fragmentation pattern with a stored library of partial spectra and identify the substance. This can be done either automatically in the selected ion monitoring mode, which offers good sensitivity, or manually through the scan mode, which offers less sensitivity but positive compound identification. The MM-1 can also be used to collect spectra of unknown substances, provided they are volatile and in sufficient quantity for the instrument to detect them. There are a number of mass spectrometers on the market; what makes the MM-1 unique is the sample inlet system and the instrument portability. For research purposes and special applications, the sample inlet probe may be replaced with a miniature gas chromatograph with a 15 meter capillary column and an injection port which accepts solid sorbent tubes. The instrument is ruggedized to military specifications and can operate while being driven in an off-road vehicle. All parameter data is stored in erasable electrically programmable read-only memory (EEPROM) and cannot be accidentally erased (such as from a power failure), though it can be manually altered. The MM-1 has been used with success in EPA-observed tests with soils and other complex sample matrices (Reference C). Specifications are given in Table 1.

C. Software Description. In addition to its unique portability and sample inlet system, the MM-1 contains programming which allows its use as a compound monitor. That is, the operator can program the instrument with spectral data from a number of compounds and the MM-1 will monitor for their presence. This data is stored in up to seven libraries of up to 60 compounds each. Only one library can be active at any time, and up to 22 compounds can be displayed on the video monitor at once. The operating system is menu-driven by computer, and is written in such a way that the number of control buttons and switches has been minimized. For each substance in its library, the MM-1 uses four mass fragments to identify and quantify it. The four fragments are chosen by a chemist using his/her knowledge of mass spectrometry to select ions which will



maximize detection sensitivity and yet minimize the possibility of interferences from other substances. Since some chemicals have similar fragmentation patterns, careful choice of fragments which give a pattern specific to that compound is necessary to insure that false detections do not occur. This data, along with some additional data which sets alarm levels and adjusts tolerance levels, is stored in the library for each compound.

An optional Compaq personal computer (PC) may be attached, allowing permanent storage of data on disk drives and remote operation from the PC keyboard. With the computer and gas chromatograph (GC) attachment, the instrument essentially becomes a laboratory-grade gas chromatograph-mass spectrometer instrument with full capabilities for such options as temperature programming, scan and selected ion modes, data storage and post-run processing, and database/library searches. Most of these functions are available in the military version without the optional equipment, but the functions are more limited and less useful.

Table 1. Specifications for MM-1 Mobile Mass Spectrometer.

Dimensions:	100 cm high X 70 cm wide X 80 cm deep.
Weight:	145 kg.
Power Requirements:	24 VDC, up to 20 A (will tolerate 20-28 VDC).
Available Items Required:	Thermal Printer Paper, Calibration Fluid, extra Silicone Rubber Sampler and Inlet Membranes.
Training Required:	Minimal; a lab tech can learn basics in a day; more complicated functions take somewhat longer.
Data Storage:	Can store in EEPROM up to 72 sampled spectra, 7 methods, 7 libraries (60 compounds each), and an error table. Optional computer can store unlimited spectra and library files.

IV. Method Development.

A. Identification of Parameters.

1. Substances Sought. In some sampling scenarios, the operator does not know what chemicals to expect. In others, a list of chemicals known to have been used in the structure is available. The latter situation applied in Building ES625, as a list of chemicals known to have been used in the building was available (Table 2), along with Material Safety Data Sheets for each compound. The list contains a wide variety of substances, from harmless nitrogen to the potentially lethal nerve agents. This list would prove a daunting challenge to most other detectors, but the mass spectrometer will detect any of them volatile enough to be vaporized and passed through the sample inlet system. This essentially means the organic compounds, and excludes most of the others. Since the bulk of the list is organic, the MM-1 will detect most of the substances if present. A number of the chemicals were initially eliminated from consideration as monitored substances for one of several reasons: the chemical was not hazardous (i.e. nitrogen); the chemical would be sufficiently volatile as to no longer be present in the building (i.e. ammonia); the chemical would not be detectable by the MM-1 due to its lack of volatility (i.e. sodium hydroxide); no reference mass spectrum could be found in the literature, nor was any of the substance available to generate a spectrum (i.e. GA hydrolysis product). The



program library on the MM-1 will hold up to 60 substances at one time (up to seven libraries may be generated and stored, though only one may be in use), so the compounds were further restricted to those thought to be possible on the fourth floor of Building E5625, where our sampling trials were conducted in the Summer of 1990.

Table 2. List of Some Substances Known to Have Been Used in Building E5625.

Diisopropylcarboiimide	Trichloroethylene (TCE)	*71840-25-0
Methylphosphonic difluoride	Methylphosphonic dichloride	Powdered Bleach (HTH)
Dimethyl polysulfide	(Poly) Isobutyl methacrylate	Ethyl acetate
Dibutylamine	Chloropicrin (PS)	Triphosgene
Potassium cyanide	Hexylene glycol	Methyl cellosolve
Tetrahydrofurfuryl alcohol	N-Methylglucamine	Carbitol
Isoamyl salicylate	B-1 Dye	Tobias acid
p-Nitroaniline	Sodium nitrite	Sulfamic acid
Sodium acetate	Ethyl cellosolve	Carbon impregnite
Carbanilide	2-Diisopropylamino ethanol	*57856-11-8
Isobutane	Methylphosphonous dichloride	Triethyl phosphite
Phosphorous trichloride	Diethylmethylphosphonite	Hydrofluoric acid
Triisopropyl phosphite	Sodium hydroxide	Acetone
Acetylene	Hydrochloric acid	Isopropanol
Isopropyl amine	Propylene glycol	Ethylene glycol
Methane	Ethanol	Nitrogen
Ammonia	Sulfur	Methylene chloride
BIS	Tabun (GA)	Sarin (GB)
Soman (GD)	*93240-66-5	*85473-32-1
GF	*85473-32-1 (trans-)	VX
BZ	*54390-94-2	*75321-25-4
Adamsite (DM)	*93101-83-8	*37830-21-0
LSD	Bromobenzyl cyanide	Levenstein mustard
HT	Distilled mustard (HD)	Nitrogen mustard
Nitrogen mustard-2	Nitrogen mustard-3 (HN-3)	Lewisite (L)
Phosgene oxime (CX)	Cyanide (AC)	Cyanogen chloride (CK)
Phosgene (CG)	*GD hydrolysis product	*2698-41-1 (CS)
3-Hydroxyquinuclidine	*GA hydrolysis product	GB hydrolysis product
Mace (CN)	*GF hydrolysis product	*VX degradation product
Cyclohexanol	2-Methyl cyclohexanol	t-2-Methylcyclohexanol
Benzilic acid	*257-07-8 (CR)	*106-52-5
4-Hydroxy-1-methylpiperidine	Pinacolyl alcohol	*20820-80-81

* - Where commonly recognized names are non-existent, either a descriptive name or the CAS Number is used to facilitate identification for the reader. Those compounds followed by their Army codes in parentheses are also found in Table 3.

2. Programming the Detector. The mass spectra for the sought substances were researched in a database published by the National Institute of Standards and Technology (Reference D). Their spectra were obtained and the major mass fragment ions were identified as to mass number and percent relative abundance (percentage of the largest mass ion in the spectrum). (Note: This phase of the research remains unfinished at the time of this writing; initial testing was done with a selection of compounds whose spectra were readily



available. Army spectra of chemical warfare agents were used as a starting point.) Table 3 lists the pertinent data in this regard for the substances sought in our preliminary testing. Four ions were chosen for each substance sought. The choice of ions to be used was a delicate matter, for the sensitivity and selectivity of the detector would be governed by the ions chosen. At least two of the ions needed to be indicative of that substance (and preferably present in no others). Ions of greater abundance gave more sensitive detections than ions of lower abundance. In some cases, compounds gave many of the same mass fragments, and the best way to distinguish them was through the use of the "impossible" ion, a fragment which must NOT be present in order for a detection to take place. Once the four ions for a substance were chosen, they were entered into the memory of the MM-1 computer controller, along with some ancillary data which helped the instrument eliminate false positive readings and set the monitor's alarm levels. MM-1 parameters chosen used are given in Table 3.

2. Quality Control Procedures. The detector used to sample a possibly contaminated building must be trustworthy; one must be able to trust negative readings as well as positive ones. Quality control (QC) samples are the way to accomplish this. Building material samples can be spiked with known quantities of a chemical and the instrument response to that chemical can be used to verify that the instrument will qualitatively identify the substance correctly and quantitatively detect the substance to a pre-determined level. If the instrument response is within a range of acceptable values for the QC sample, then the responses for the other substances (or lack of responses) can be trusted to be accurate.

a. Choice of Spiking Substance. Three readily available substances were tried for spiking QC samples: 1,1,1 trichloroethane, dimethyl methylphosphonate, and methyl salicylate (MeS). All were readily detectable, but methyl salicylate (oil of wintergreen) was chosen as the best of the three due to its lower volatility and ease of handling, and the similarity of its vapor pressure to that of distilled mustard (HD), a chemical warfare agent.

b. Spiking Procedure. Solutions of MeS were made in methanol for use in spiking operations. Methanol was chosen due to its low molecular weight (32 daltons) and corresponding non-interference with detection of sought substances. By choosing the proper solution and using a microliter syringe, the operator could apply MeS in any quantity desired, in our trials through the range of nanograms to micrograms. A chalk circle was drawn on the selected location and the MeS solution applied to the center of the circle. The bulk of the methanol evaporated within seconds and the location was then ready for sampling. The MM-1 sampler was placed over the spiked spot and held in contact with it for 10 seconds, after which it was removed. The MM-1 display was then observed for a response for up to 30 seconds. The level of response was then recorded. As a control, small pieces of paper towel were similarly spiked and placed in a glass Petri dish, then sampled likewise. This allowed operators to determine what the response would be under ideal conditions, as compared to the less than ideal concrete surfaces.

3. Sampling Procedure. The sampling procedure was identical to the spiking procedure, without the spike, of course. The MM-1 sampled for 10 seconds, then was observed for 10-30 seconds more for a response. If there was no response, the MM-1 was then ready for the next sample. Theoretically, samples could be taken at a rate of about 60 per hour, though in practice about



15 per hour was the maximum possible due to administrative tasks (recording data, marking the sites, moving the detector, etc.). Still, quite a number of samplings could be accomplished in a single day in this manner. Sites which returned a positive reading were noted, and were returned to later for more in-depth sampling, with the intention of finding the extent of the contamination and mapping it, if possible. Note: During such sampling, should a site heavily contaminated with compounds of low volatility (such as greases or oils) be sampled, it is possible that these compounds could contaminate the sampling membrane or sample line, causing a high background level of mass fragments. After incorporating these fragments into a new background reading, sampling may continue with the MM-1, but instrument sensitivity may be lessened. Programming the instrument for a bake-off (lasting anywhere from 30 minutes to overnight) generally solves this problem, but sampling must be discontinued during the bake-off period.

V. Summary of Data from Building E5625 and Related Laboratory Studies.

Building E5625 was visited twice during Summer 1990; both times, sampling trials were limited to the fourth floor, as work to clean up the other floors was ongoing. The first visit was used to establish quality control procedures, the second to conduct some trial sampling using procedures developed in the laboratory. Both trials were preliminary in nature, and the data therefore does not represent any official Army position. Subsequent discovery of asbestos in the building prevented further efforts, though it is expected that this problem will be resolved and data collection may continue sometime in mid-1991.

A. Quality Control Samples. After the choice of MeS as the spiking material, trials were held to establish the detection limit for MeS on the structural surfaces, which on the fourth floor of E5625 were unpainted concrete. As a control, droplets were also applied to paper towels on glass plates. The controls regularly detected quantities of MeS in the range of 1-10 ng MeS. On the concrete, the range was from 100-500 ng MeS. This was probably due to two phenomena: the MeS soaked into the concrete somewhat; the irregular bumpy surface of the concrete prevented the sampling membrane from making intimate contact with the MeS. This may prove to be the greatest difficulty in using the MM-1 to sample irregular surfaces; if the chemical does not contact the sampling membrane directly, detection sensitivity falls off dramatically. Also, samples in porous matrices such as concrete cannot be sampled with the MM-1 below the surface; the surface layer must be removed through drilling or otherwise breaking the substrate in order for the MM-1 to get at embedded materials. Of course, this same problem exists for other sampling methods.

B. Surface Sampling Trials. Once a method was established, the fourth floor was sampled while monitoring for MeS and a number of chemical agents. Twenty-four locations were sampled throughout the floor; nothing was detected. The unconfirmed presence of hydrocarbons (oils, greases, etc.) was found at one location, but otherwise the detector produced no responses. Quality control samples consistently produced detections for MeS to the 100 ng level, but no other detections occurred. This means that the sampled locations were clean and free of contaminants, at least to the microgram level, on the concrete surface. These were not surprising findings, as one would not expect to find such sub-



Table 3. MM-1 Parameters for Building E5625 Chemicals.

CRDEC Number	MM-1 Number	CRDEC Code	Mass Rel. 1 Int.	Mass Rel. 2 Int.	Mass Rel. 3 Int.	Mass Rel. 4 Int.	Warning Level	Alarm Level	Interfer- ence	Relia- bility
2	52	TCE	134 35.9	132 99.9	130 99.9	164 0.0	.6	1.5	1.5	4
11	18	PS	82 21.6	117 99.9	119 92.8	81 0.0	.6	1.7	1.3	4
53	1	GA	162 31.1	133 41.6	70 80.5	43 99.9	.6	1.2	1.3	4
54	2	GB	125 38.8	99 99.9	81 12.9	85 0.0	.6	1.1	1.3	4
55	3	GD	82 55.9	99 99.9	126 92.8	85 0.0	.6	1.0	1.3	4
56	4	GF	54 64.7	67 92.8	99 99.9	85 0.0	.6	1.1	1.3	4
60	5	VX	127 15.0	114 99.9	79 20.1	85 0.0	.6	1.0	1.3	4
62	11	DM	167 74.9	242 99.9	277 41.6	166 25.0	.6	1.2	1.3	4
70	8	HT	125 38.8	123 99.9	109 0.0	83 0.0	.5	1.1	1.3	4
71	7	HD	158 20.1	109 99.9	160 4.9	111 38.8	.6	1.1	1.3	4
74	9	HN-3	92 44.8	156 64.7	154 99.9	85 0.0	.6	1.1	1.3	4
75	14	L	206 51.9	145 99.9	110 92.8	208 51.9	.6	1.2	1.1	4
76	19	CX	115 64.7	113 92.8	78 99.9	71 0.0	.6	1.0	1.3	4
77	15	AC	26 12.9	27 99.9	43 0.0	57 0.0	.6	1.8	1.3	4
78	17	CK	63 35.9	61 99.9	35 12.9	71 0.0	.6	1.8	1.3	4
79	16	CG	65 35.9	63 99.9	98 10.4	109 0.0	.6	1.8	1.1	4
80	23	CN	154 8.4	105 99.9	77 60.1	85 0.0	.6	1.4	1.3	4
81	24	CS	188 25.0	153 99.9	190 8.4	126 31.1	.6	1.1	1.3	4
82	25	CR	167 51.9	195 99.9	166 20.1	139 15.0	.6	1.3	1.3	4

Note: Missing compounds from this table indicate that the compound is not yet included into an MM-1 method.
For identification by common name or empirical formula, see Table 1.

stances on the surface of a floor which had not been used in years. It WAS surprising that more detections for grease or oil had not been found; one would suspect that normal work habits would produce such substances from spills, soles of work shoes, tools, etc.

C. Air Sampling Trials. One of the rooms on the fourth floor smelled strongly of sulfurous compounds, so an attempt was made using sorbent tubes to sample the air and identify the source of the odor. Tubes were fabricated using charcoal, Tenax-GC, and Chromosorb 106 as packing materials. They were then allowed to aspirate the air in the room for periods ranging from a few hours to overnight. No useful results were obtained with the Chromosorb 106, though the Tenax-GC and charcoal produced gas chromatograms containing some small peaks. The GC peaks obtained were too small to produce positive identifications, but polysulfides, hydrocarbons, and phthalates were indicated by the spectra obtained. Phthalates are often used as plasticizers in plastic tubing, hydrocarbons are ubiquitous in industrial sites, and polysulfides are among the chemicals used in the building. Much more work is needed to optimize the tube and analytical parameters to be used before this can be a reproducible and quantifiable technique.

VI. Summary.

Structures which have been contaminated with hazardous chemicals pose a threat to public health and the environment. Destruction of such structures and disposal of the rubble can be dangerous and costly without first sampling the building materials for the existence of the hazardous chemicals. Such sampling can be costly and time-consuming using existing methods. The German Army has developed a mobile mass spectrometer for use as a battlefield chemical agent detector. This detector, an electron-impact type quadrupole mass spectrometer, can be programmed to simultaneously detect all types of volatile industrial chemicals as well as chemical warfare agents. It therefore shows much promise as a sampling device which can provide real-time data concerning the existence of suspected hazardous chemicals on structural surfaces.

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AN EVALUATION OF HEADSPACE GAS CHROMATOGRAPHY FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN SOIL

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INTRODUCTION

Volatile organic compounds (VOCs) are the most frequently encountered contaminants at hazardous waste sites (Plumb and Pitchford 1985). During the investigation and remediation of these sites, surface and vadose zone soil samples are collected and analyzed for the VOC priority pollutants. Traditionally, VOC samples were collected as bulk soil samples from which subsamples were taken in the laboratory for analysis as prescribed by the Environmental Protection Agency's (EPA) SW-846 methods document. Lewis et al. (1991) in a recent EPA report recommended that soil samples be placed directly into a specially designed analysis vessel or an appropriate bottle containing methanol (MeOH) upon collection in the field to prevent the losses incurred due to volatilization when a soil is disturbed (i.e. transferred from one vessel to another). This publication also provides guidance on how to limit biodegradation losses of VOCs during the allowable storage period. These recommendations will improve the quality of VOC determinations in soil samples analyzed for litigation compliance by the purge and trap (PT), gas chromatograph (GC), or gas chromatograph/mass spectrometer (GC/MS) EPA analysis procedures. A problem that was not addressed is how to reduce the number of uncontaminated samples sent for costly laboratory analysis.

Field screening methods can be used to select samples for in-depth laboratory analysis, thereby controlling the number that are suspected to represent background concentrations (blanks). Field methods also allow for timely decisions to be made on site (Spittler et al. 1985, Marrin 1985). From its inception, field screening using headspace sample preparation and analysis with a portable gas chromatograph (HS/GC) eliminated the storage and transfer problems now recognized by the EPA (Lewis et al. 1991), and filled an essential need between litigation quality analysis of discrete soil samples and the initial screening for VOCs that is often performed with hand-held sniffers and/or soil gas measurements. These preliminary field screening methods that can directly measure local vapor concentration, although useful in delineation of highly contaminated areas, have been shown to be unreliable indicators of soil-bound VOC concentrations (Smith et al. 1990).

Surely, the EPA laboratory analysis procedures were never intended for, and would be too time-consuming and expensive for field screening of discrete soil samples. Headspace sample preparation followed by analysis with a portable GC is both a rapid and economical method for the analysis of VOCs in soil samples. This screening method has shown comparable results to PT/GC for the determination of VOCs in aqueous samples (Dietz and Singley 1979). However, with regard to soil samples, this comparison has only been made after artificial treatments, or under conditions where critical variables, such as holding time, were not held constant between the two methods being compared (Hewitt et al. 1991).

A meaningful statistical comparison of analytical methods for VOCs in soil has been obtained using a vapor exposure method for introducing VOCs to soils in the laboratory (Jenkins and Schumacher 1987, Hewitt et al. 1991). This fortification technique, analogous to the exposure of unsaturated soils above contaminated groundwater, has shown excellent precision among replicate laboratory samples. The compounds chosen in these initial studies were trans-1,2-dichloroethylene (TDCE), trichloroethylene (TCE), benzene (Ben), and toluene (Tol). These compounds are representative of the constituents commonly found in refined petroleum products and chlorinated solvents.

Our study compares the levels of four selected VOCs in two laboratory-treated soils, and TCE concentrations in field samples, as determined by HS/GC/photoionization detection (PID) and PT/GC/MS. The field soils were obtained from two different sites where exposure to TCE has occurred over the past 20 years. The HS sample preparation and analysis used was streamlined for field applications and uses water to extract VOCs, whereas the PT/GC/MS method follows the guideline provided in SW-846 for Method 8240 and uses an MeOH extraction. Overall, this comparison of methods involves the following operational variables: extraction solvent (methanol vs water), solvent/vapor phase partitioning (static vs dynamic), and method of detection. Since both the solvent/vapor partitioning and method of detection are internally consistent (samples and standards are treated identically) they should not affect the intermethod comparison, but mainly influence the precision of each respective method. Thus, this comparison will primarily focus on



the difference between methanol and water as extractants of soil-bound VOCs.

EXPERIMENTAL

A brief outline of the experimental procedure is presented here. A more complete description of the laboratory vapor contamination method, analysis technique, and instrumental parameters has been reported elsewhere (Hewitt et al. 1991).

Laboratory-fortified and field samples

The two soils used with the vapor fortification treatment were obtained from the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA, standard soil No. AO46) and from Point Barrow, Alaska. Characteristics of these soils are listed in Table 1. Prior to vapor contamination no VOCs were detectable in either soil used. Separate 2.0-g subsamples of each soil were placed into 40-mL glass vials (VOA vial) equipped with Teflon-faced silicone rubber septa and open-faced screw caps. The vials were left uncapped in a desiccator with 50 mL of an exposure solution containing TDCE, TCE, Ben, and Tol in an open petri dish (Fig. 1). Vials with no soil were

included to check for sorption onto the inner glass surface of the vial. The treatment periods in the vapor exposure chamber were 4 and 39 days. Soil-bound VOC concentrations ranging from 100–3000 $\mu\text{g/g}$ were obtained after soils were exposed in this fashion to the vapor generated from the following solution: 1.4 mL Tol (1.21 g), and 0.4 mL of each TDCE (0.503 g), TCE (0.586 g), and Ben (0.351 g) taken to a 100-mL volume in MeOH. Concentrations near the likely cleanup action level (e.g. 1–200 $\mu\text{g/g}$) were obtained by exposing the soils to the vapor above a 1:1 dilution of the above MeOH solution with tetraethylene glycol dimethyl ether (tetraglyme).

After the specified exposure periods, two sets of triplicates of each soil type and two empty VOA vials (blanks) were taken out of the desiccator. The removed vials were then aspirated for ten minutes by placing them along the front edge of an exhaust hood. This step is necessary since the vapor concentration of the VOCs in the desiccator during exposure is in the high parts-per-thousand (v/v) range, whereas the levels established for the soil ranged from the high to low parts-per-million (wt/wt). The ten-minute aspiration used for these tests lowered the VOC concentrations obtained for the empty VOA vials below detection limits. Following aspiration, the appropriate extractant was added and then the vials quickly capped.

The two field samples used in this study came from two different sites where TCE contamination originated some 20 years ago. One site was the Cold Regions Research and Engineering Laboratory (CRREL), where samples were collected with a Veihmeyer tube 3 feet below the ground surface. The other sample was provided as a bulk soil sample (≈ 30 g), through a cooperative effort with Clarkson University, and was used in the study of Pavlostathis and Jaglal (1991). Henceforth, this soil will be referred to as the Clarkson soil. For each method comparison ten subsamples were taken from the 15-cm-long by 2-cm-diameter cores collected at CRREL, and six from the bulk soil sample shipped to our laboratory. Both soils were rapidly subsampled once opened to the atmosphere, and the subsamples randomly placed in pre-weighed VOA vials, half containing water and half containing MeOH. Soil characteristics were not determined for the CRREL soil, but have been established for the soil received from Clarkson (sand 56%, silt 32%, clay 12%, moisture 22%, and total organic carbon 0.13%).

Extraction of soil-bound VOCs

The HS/GC/PID sample preparation and analysis procedure followed the work of Dietz and Singley (1979) and recommendations of T.M. Spittler (personal communication, 1989). Samples and blanks were extracted with 30 mL of deionized water (Type 1, Millipore Corp.). Equilibrated headspace concentrations were developed

TABLE 1. Characteristics of soils contaminated by vapor exposure.

Characteristic	USATHAMA standard soil	Point Barrow, Alaska, soil
% organic carbon	1.45	6.69
% clay	53.6	20.1
% moisture	1.43	2.00

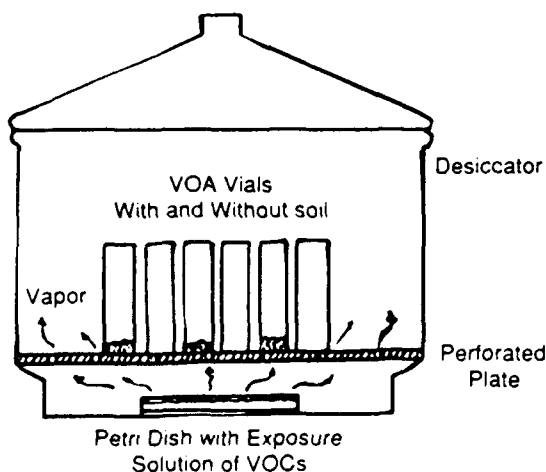


Fig. 1. Vapor contamination chamber.

by vigorously shaking the sealed vials for two minutes (by hand), or in the case of the field-contaminated sample received from Clarkson, until the soil was physically dispersed. The sample preparation protocol for PT/GC/MS procedure followed EPA SW-846, Method 8240, for high level soil concentrations. The only deviation from SW-846 guidelines was the doubling of sample weight and corresponding MeOH volume for extraction.

Standards

The combined analyte solution prepared for the vapor fortification treatment also served as the analytical stock standard. Preparation of this stock solution involved volumetric transfers with glass pipettes, checked gravimetrically, as each analyte was added to a 100-mL volumetric flask partially filled with MeOH. When calibrating for analyses in the 100- to 3000- $\mu\text{g/g}$ concentration range, the stock solution served as the working standard. A ten-fold dilution with MeOH was performed for analyses in the 1- to 200- $\mu\text{g/g}$ range (Table 2).

Analysis

All samples were analyzed immediately after extraction, except in the case of the second comparison performed with the TCE-contaminated soil sent to our laboratory. In this instance instrumental problems caused analysis to be performed on the following day. Due to the length of analysis time required by PT/GC/MS, the statistical comparison for both methods was based on a single determination for each subsample (which is common practice for actual analysis).

1. Headspace/GC/PID analysis

Headspace gas chromatography was performed on a Photovac GC (Photovac, Inc., Model 10S10) equipped with a photoionization detector (Fig 2). A rapid analysis

with baseline resolution between the four test analytes (TDCE, Ben, TCE, and Tol) was achieved with a packed column of 10% SE-30 on Chromosorb 80/100 mesh, 30-cm length, 0.32-cm O.D. The carrier gas was zero grade air flowing at 15 mL/min. All chromatography was performed at room temperature ($\approx 24^\circ\text{C}$). Volumes of equili-

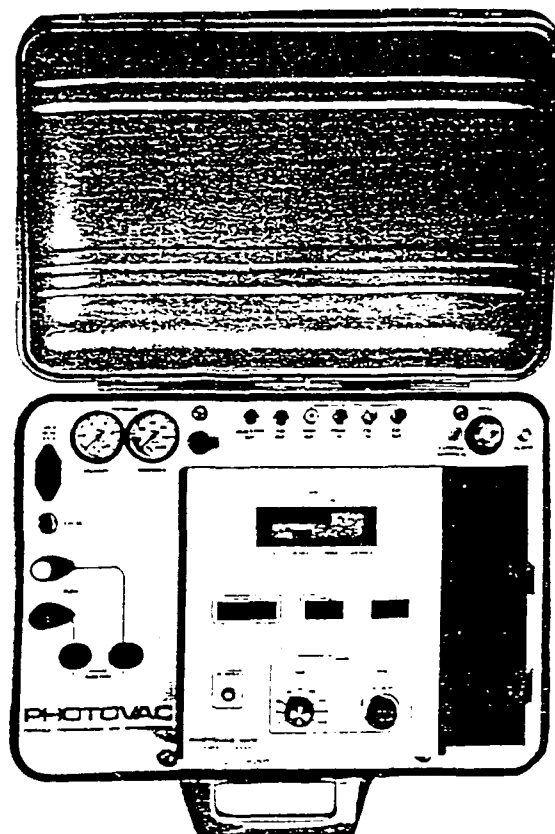


Fig. 2. Photovac GC equipped with photoionization detector.

Table 2. Stock standard concentration and volumes used for the different ranges of expected VOC concentrations in the soil.

<i>Working standard</i>	<i>Vol. of working std. used for calibration</i>	<i>Vol. of MeOH extract or headspace used for analysis</i>	<i>Concentration range</i>
HS/GC/PID			
1/10 Stock	10–80 mL	25 mL	1–200 $\mu\text{g/g}$
Stock	50–200 mL	2 mL	100–3000 $\mu\text{g/g}$
PT/GC/MS			
1/10 Stock	10 mL	100 mL	1–200 $\mu\text{g/g}$
Stock	10 mL	10 mL	100–3000 $\mu\text{g/g}$

All stock solutions were refrigerated at 4°C and remade on a monthly basis. Dilutions of stock solutions were prepared on the same day they were used.



brated headspace vapor analyzed ranged between 2 and 25 mL (Table 2) for the high and low concentration samples, respectively. Transfers were made with gas-tight syringes (Hamilton). Under these operating conditions the approximate retention times for the compounds were 0.86 min TDCE, 1.8 min Ben, 2.6 min TCE, and 4.8 min Tol. Thus, repetitive analyses could be performed every 6 minutes. Analyte responses were recorded as peak heights on a field-portable strip chart recorder (Linear Instruments). This portable GC and recorder can run on internal DC power and internal gas supply for approximately eight hours. It costs less than \$15,000 and requires minimal training for operation.

2. Purge and Trap GC/MS analysis

Purge and trap analysis was performed with a Tekmar liquid sample concentrator (LSC-2) coupled with a model ALS automatic laboratory sampler. Analyte separation and detection was performed on a Hewlett-Packard 5890 series II GC interfaced to a Hewlett-Packard series 5970 mass selective detector, mass spectrometer. Samples were prepared for purge and trap analysis by filling a 5-mL Hamilton syringe with 5.0 mL of bubble-free distilled water, adding a 10-mL aliquot of the deuterated benzene internal standard (0.425 µg/g), and then adding a 10- or 100-mL aliquot of the MeOH sample extract, for the high and low concentrated samples, respectively (Table 2). Both the internal standard and the MeOH extracts were transferred with syringes (Hamilton). The prepared sample with internal standard was then transferred to a purge chamber. Repetitive analyses were performed at a rate of one per hour.

RESULTS AND DISCUSSION

Results from the intermethod comparison for the laboratory vapor-fortified soil can be found in Table 3. This table includes the means and standard deviations of the analysis of triplicate subsamples over two exposure periods at the two vapor treatment concentrations. Table 4 shows the results obtained for the field-contaminated soils collected from the two sites where long-term exposure to TCE had occurred. Mean concentrations were compared using the *t*-test after determining if the variances were homogeneous with the *F* ratio. If variances were non-homogeneous, the larger variance was used for both means in the *t*-test comparison. Both statistical tests were performed at the 95% confidence level.

The laboratory treatment of the USATHAMA standard soil frequently showed no significant difference in the mean concentrations obtained by the two methods for all four of the VOCs determined. And more than half of the concentrations established for TDCE and Ben were not statistically different regardless of exposure solution, soil, and treatment period. The most frequent statistical difference found by this intermethod comparison was observed for TCE and Tol concentrations determined in the Point Barrow, Alaska, soil. The 6.69% organic carbon in the Point Barrow soil represents a "worst" case in terms of low HS analyses. The two compounds in this treated soil, TCE and Tol, that showed significantly greater levels as determined by the EPA method have the largest octanol/water partition coefficients of the VOCs tested (*K*_{o/w} (mL/mL): Ben 117, TDCE 120, TCE 195, Tol 550). The observation that these more hydrophobic VOCs

TABLE 3. Intermethod comparison of VOC soil concentrations (µg/g) for the laboratory vapor exposure treatments.

	Low Vapor Concentration Exposure (µg/g)				High Vapor Concentration Exposure (µg/g)			
	4 days exposure		39 days exposure		4 days exposure		39 days exposure	
	HS/GS	PT/GC/MS	HS/GC	PT/GC/MS	HS/GS	PT/GC/MS	HS/GC	PT/GC/MS
USATHAMA standard soil								
TDCE	1.63±0.11†	1.84±0.66*	1.71±0.15	4.93±1.34	72.8±5.89	66.0±2.65*	134±11.0	122±18.7*
Ben	8.75±0.19	5.67±1.30	8.75±0.09	7.33±1.42*	117±6.51	94.3±2.17	184±4.04	177±34.1*
TCE	11.7±0.40	9.22±1.68*	11.6±0.29	15.1±2.41*	214±9.81	202±15.9*	372±9.50	380±105*
Tol	42.9±1.50	33.3±3.79	43.4±2.21	41.4±4.90*	492±20.8	529±55.8*	885±50.0	1660±427
Point Barrow, Alaska, soil								
TDCE	12.3±0.40	12.5±1.76*	11.7±0.70	19.1±0.70	148±4.00	170±9.71	225±10.4	230±12.1*
Ben	29.1±2.87	22.0±3.00	26.7±0.29	26.0±1.94*	198±10.4	204±5.00*	256±14.0	281±32.0*
TCE	34.1±2.87	39.0±1.78	34.2±0.35	55.0±2.26	319±27.1	444±12.5	416±23.6	613±56.9
Tol	87.8±9.59	116±8.33	96.2±1.15	134±8.08	689±76.3	1120±5.77	927±62.9	2740±61.1

† Mean and standard deviation (µg/g) for triplicate samples

* HS/GC and PT/GC/MS analyses were not statistically different at the 95% confidence level.



TABLE 4. Intermethod comparison of TCE soil concentrations ($\mu\text{g/g}$) for field samples.

		<i>TCE concentrations ($\mu\text{g/g}$)</i>	
		<i>HS/GC</i>	<i>PT/GC/MS</i>
CRREL soil			
First set			
Subsamples		18.3, 11.4, 6.47, 3.60, 10.7	83.5, 3.31, 28.7, 4.33, 2.51
		$10.1 \pm 5.58^\dagger$	$24.5 \pm 34.8^*$
Second set			
Subsamples		4.3, 9.00, 4.86, 12.3, 16.8	4.40, 11.7, 36.0, 45.5, 36.9
		11.4 ± 4.66	$26.9 \pm 17.8^*$
Clarkson Soil			
First set			
Subsamples		3.83, 3.44, 4.17	8.77, 9.89, 11.5
		3.81 ± 0.37	10.0 ± 1.37
Second set			
Subsamples		3.45, 3.54, 3.81	7.87, 7.71, 8.07
		3.60 ± 0.19	7.88 ± 0.18

† Average and standard deviation.

* HS/GC and PT/GC/MS analyses were not statistically different at the 95% confidence level.

were not recovered from the Point Barrow soil partitioned with water to the extent of what was recovered with an MeOH agrees with previous works (Karickhoff et al. 1979, Chiou et al. 1983, Kiang and Grob 1986, Boyd and Sun 1990) that have addressed the effect of soil organic matter concentration on partition coefficients.

The results from the two field-contaminated soils address another aspect that needs consideration and also demonstrate a weakness common to many of the previous method comparisons. Comparison of the average TCE concentrations shows an apparent difference between methods of a factor $>2\times$. This difference in concentration has previously been attributed to kinetic differences between a water and MeOH extraction when analyzing for VOCs in low organic carbon soils that have experienced long term exposure (Smith et al. 1990, Sawhney and Gent 1990, Pavlostathis and Jaglal 1991). Even though the comparisons were performed on five subsamples of the CRREL soil, and on triplicates for the Clarkson soil, only the latter showed a statistical difference for the mean TCE concentrations determined. Clearly, the variability in TCE concentration from subsample to subsample in the CRREL soil, which is typical of many environmental samples, would compromise any intermethod comparison, particularly if only split samples were used. Thus, frequently the effect of total organic matter present in a soil and/or the history of a sample can not be rigorously demonstrated with field samples.

This analysis of the concentrations established by the two methods probes beyond the objective of field screening, which is to identify the presence and approximate amount of a constituent, and reveals some of the limitations of the aqueous headspace sample preparation procedure as compared to this EPA method. Overall, the agreement between the two methods for determining VOC concentrations in soils was good for both the laboratory and field samples. With regard to using a water extraction HS sample preparation and portable GC analysis to screen samples, this technique never produced a false negative determination. Also the methods showed parallel trends for the laboratory-introduced soil-bound VOCs with regard to the vapor treatment concentration, concentration of soil organic matter, and exposure period. The largest discrepancies in concentrations for this intermethod comparison occurred for a soil with unusually high organic carbon content, and for a low organic carbon soil that was exposed to VOC contamination for 20 years. Even in these two extreme cases water extraction-HS/GC analysis provided concentration estimates that were better than 30% of the concentration determined by the EPA methanol extraction-PT/GC/MS method. On the other hand, this analysis indicates that for soils with low organic carbon content that have experienced only short-term exposure to VOCs, these two methods of analysis will provide results that are not statistically different at the 95% confidence level.



CONCLUSION

Compared to EPA Method 8240 for high level VOCs, a water extraction HS sample preparation and portable GC analysis for VOCs in soils is quicker, more field compatible and economical, and requires no use of hazardous chemicals in the field. This latter procedure is particularly useful as a field screening method, minimizing sample handling and lag time between collection and analysis and thereby reducing the possibility of false negatives that has plagued soil samples that were stored and handled prior to analysis. As with any field method, limitations need to be clearly established so that the results are appropriately applied. However, with regard to soil sample screening, aqueous HS sample preparation and portable GC analysis provide a valuable tool, allowing for a better utilization of analytical resources and funds for the assessment and remediation of hazardous waste sites. Use of this field screening method would greatly reduce costs and analysis time, and potentially increase the reliability of soil VOC determinations.

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Acknowledgments

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THE PHYSICAL PREPARATION AND CHEMICAL ANALYSIS OF SOIL/COMPOST SAMPLES

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Historical production of conventional munitions by the U.S. Army has led to the contamination of soils with explosives at several sites in the United States. Estimates put the contamination level at approximately 1 million tons, and the cost of treatment using existing technology (incineration) at over 1.5 billion dollars. Due to this high cost, research efforts in soil decontamination have focused on the development of cost-efficient alternatives. One area of research which has shown initial success is the composting of contaminated soils with organic matter (animal manure, forage, wood products, etc.). In initial experiments several parameters were studied to determine the optimal conditions for composting. These include soil/compost ratio, time of composting, composting temperature and analytical methods used to extract explosives. Initial results indicated that concentrations of the principal explosives, 1,3,5-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), were reduced 85-99% by composting, but information on the optimal conditions were confounded by large errors (greater than 100%) in experimental reproducibility. These errors were attributed to variations in the physical preparation and extraction of soil/compost samples.

To correct sample preparation problems, scientists from the U.S. Army, Roy F. Weston, Inc., and the U.S. Geological Survey developed an alternative procedure for soil/compost preparation. In this procedure, samples were dried at room temperature for 24 hours, and then macerated using a Thomas-Wiley mill (model No. 4). The mill contains a series of stainless steel blades (7.5 cm wide) which rotate in a counterclockwise direction on a central hub, cutting the material against sets of stationary blades. The material is constantly processed until it passes a 2 mm screen located at the bottom of the sealed chamber. After all the material is processed, a representative sample is obtained using a Jones (riffle) splitter. The splitter consists of a series of six adjacent metal chutes which are alternately oriented 180° from each other and transfer material into two receiving containers located below and on either side of the splitter. Several liters of material can be split at one time, and a final representative sample obtained by processing material collected from only one side of the splitter.

*Use of trade names is for descriptive purposes only and does not constitute an endorsement by the U.S. Geological Survey



The degree of homogeneity was tested through a series of experiments which quantified the inorganic and explosive content of the processed material. Initial studies examined major and trace element content in 3 subsamples of uncontaminated soil/compost material using ashed sample material, a multiacid total digestion, and multi-element ICP analysis. Studies were performed using the experimental design described in Figure 1.

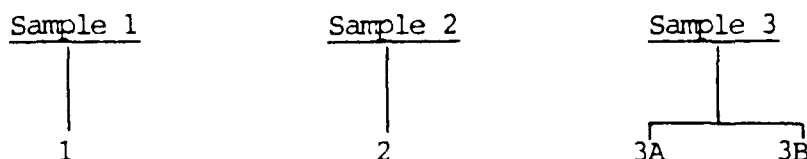


Figure 1 Experimental Design for Inorganic analysis

Analytical results for samples 1, 2, and 3 (average of 3A and 3B) represent between sample variation, while data for samples 3A and 3B reflect within-sample variation due primarily to sample processing. Results for selected elements, corrected to dry weight, are presented in Table 1.

Table 1. Total element concentrations in soil/compost samples

Element	<u>Between-sample</u>		<u>Within-sample</u>	
	<u>Avg.¹</u>	<u>%RSD²</u>	<u>Avg.¹</u>	<u>%RSD</u>
Al	20000	5.4	19000	1.2
Ca	13000	4.0	12000	0.8
Ba	216	4.2	207	0.9
Cr	15	8.5	14	0.3
Mn	310	2.9	303	0.7
Zn	54	1.8	53	0.5

1 Concentrations in ppm, dry weight

2 %RSD, percent relative standard deviation

It is apparent from Table 1 that average concentrations of inorganic constituents for between-sample and within-sample tests are similar. It is also apparent that analytical reproducibility (%RSD) is consistently better for the within-sample experiment. This suggests that the proposed preparation procedures successfully produced homogeneous sample and representative sample splits.

In the second study, contaminated and uncontaminated sets of soil/compost mixtures were analyzed for TNT content using the proposed preparation procedure. The experimental format (Figure 2) was designed to compare



within-sample and between-sample results. The experiments also examined the possibility of sample cross-contamination by alternately processing contaminated and uncontaminated samples through the Thomas-Wiley mill. The Thomas-Wiley mill was cleaned between samples using acetone.

In this experimental design, analytical results for samples CS1 and CS2a represent between-sample variability, and results for samples CS2b and CS2c represent within-sample variation for contaminated samples. For the uncontaminated samples, results for US1 and the average of US2a and US2b represent between-sample variation, and results for US2a and US2b represent within-sample variation. Analytical results for both sample types are presented in Table 2.

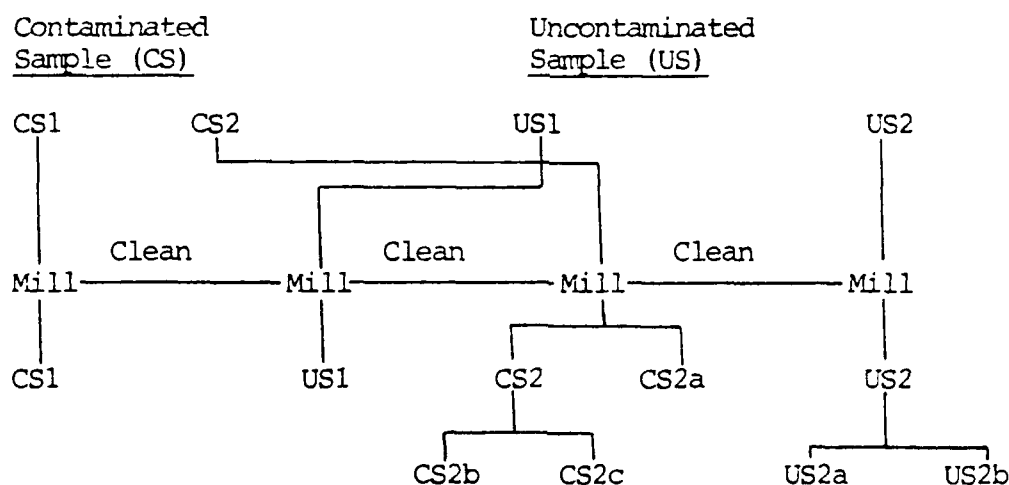


Figure 2 Experimental design for TNT analysis in contaminated (CS) and uncontaminated (US) soil/compost samples.

Results shown in Table 2 mimic the inorganic results (table 1) in that between-sample variation (11% RSD) is greater than within-sample variation (3% RSD). Also significant is the low concentration of TNT in uncontaminated samples, (less than 190 ppm), indicating that cross-contamination problems are minimal if proper cleaning procedures are followed.

Table 2. Concentration of TNT in contaminated and uncontaminated soil/compost mixture

<u>Sample Type</u>	<u>Within-sample</u>		<u>Between-sample</u>	
	Average <u>[TNT]¹</u>	<u>%RSD²</u>	Average <u>[TNT]¹</u>	<u>%RSD²</u>
Contaminated (CS)	2940	3	3200	11
Uncontaminated (US)	<190	*	<190	*

* Not calculated, all data below determination limits

1 Concentration in ppm

2 %RSD, relative standard deviation

This study identifies a sample preparation procedure for soil/compost mixtures which produces samples of excellent homogeneity. The procedure represents a significant improvement over earlier sample preparation methods, and allows scientists to more accurately monitor the decomposition of explosives in the soil/compost material.

PORTABLE DUAL WAVELENGTH ANALYZER FOR DETECTION OF TNT IN GROUND WATER USING FIBER OPTICS

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ABSTRACT

A battery-powered light-weight instrument was developed for the detection of TNT in ground water. An optrode using a membrane sensitive to 2,4,6-trinitrotoluene (TNT) was used in conjunction with a broadband light source and two optical receivers with bandpass filters (520 nm and 690 nm) as the sensing portion of the instrument. The membrane is made of polyvinyl chloride that has been doped with an amine that reacts with the TNT. The control and analysis system are built around a microprocessor-based datalogger and keypad. TNT levels down to sub parts per million can be detected.

1. INTRODUCTION

The goal of this project is to develop a portable system for in situ optical detection and estimation of 2,4,6-trinitrotoluene (TNT) in groundwater.

Previously the University of New Hampshire reported that plasticized polyvinyl chloride (PVC) membranes containing primary and secondary amines react with aqueous TNT to form a brown product which can be detected through fiber optics (Zhang et. al. 1988a). Membranes have since been developed with vastly improved stability (Zhang et. al. 1988b).

Using this membrane we set forth to develop a system for the detection of TNT. The system developed consists of two parts, the basic instrument and the sensor head.

2. INSTRUMENT DESIGN

It was decided early on to use two different wavelengths of light and ratio their outputs. The wavelengths chosen are 520 nm being absorbed by the sensor and 690 nm passing through the sensor (figure 1). By forming the ratio of the two signals, we have a self referencing system and most of the problem variables such as, changes in source intensity, coupling losses, and turbidity of the water are canceled out.

The first approach was an analog system with a bi-colored LED as the source. This system used a clock driving a flip-flop whose outputs were used to drive the led (though a pair of drivers) and to trigger a pair of sample and hold

amplifiers on the photo-amplifier output. These sample and hold amplifiers, one holding the green signal and the other the red, were connected to an analog multiplier/divider (IH6108) chip which in turn supplied the signal to a digital display.

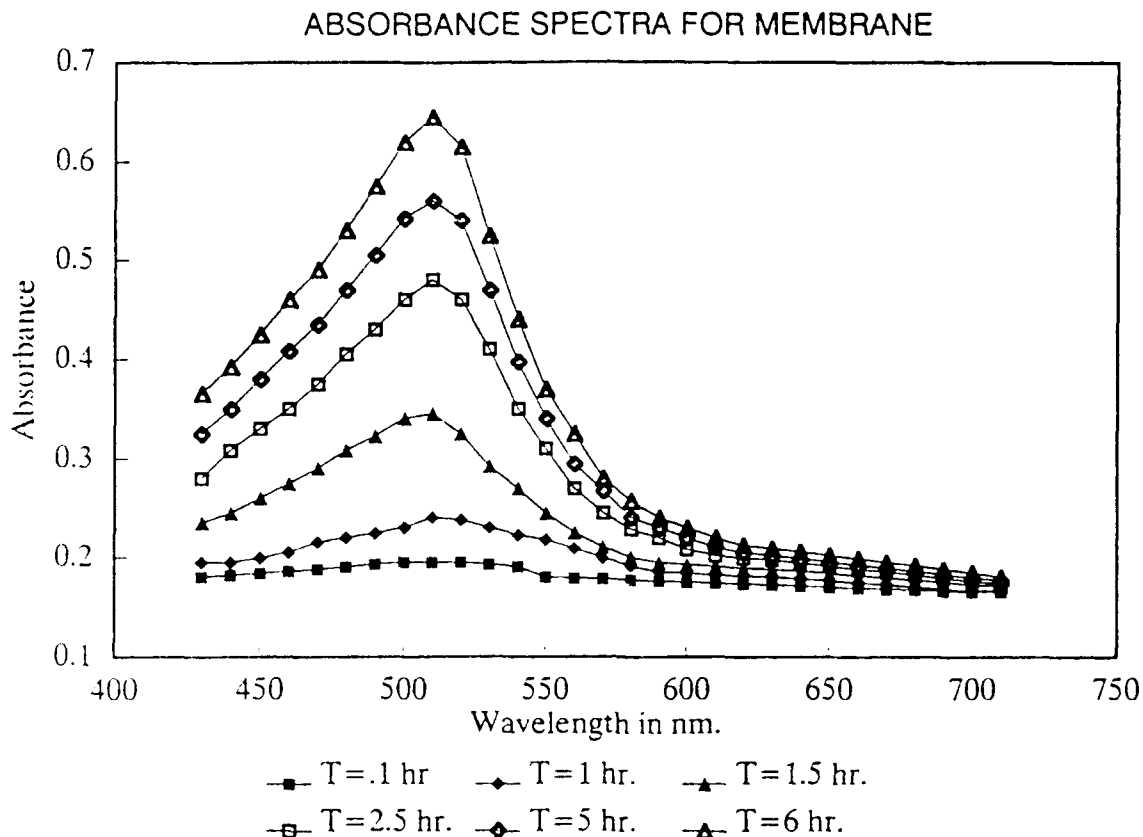


Figure 1. Absorption spectra of membrane to TNT over a six hour period.

This system had the advantage of being placed in a handheld package and powered by one 9 volt battery. Unfortunately the wavelength of the green led proved to be too long for this system to work. A variety of other light sources including electroluminescence and frequency doubling a laser were then investigated, but they did not provide enough light (electroluminescence) or as with the laser were not portable enough.

It was then decided to use a single light source of white light (75 watt projection lamp) and a pair of detectors with optical bandpass filters as the receivers (Devar Corp. type 529 series photo detector with amplifier and optical bandpass filter). It was also decided to replace the pure analog system with a microprocessor based datalogger. In this case a Tattle-Tale IVA datalogger from Onset Corp. and a keypad with display from QSI Corp. This datalogger is programmable in Basic and has an onboard 12 bit A-D converter. A block diagram of the current configuration is show as figure 2.



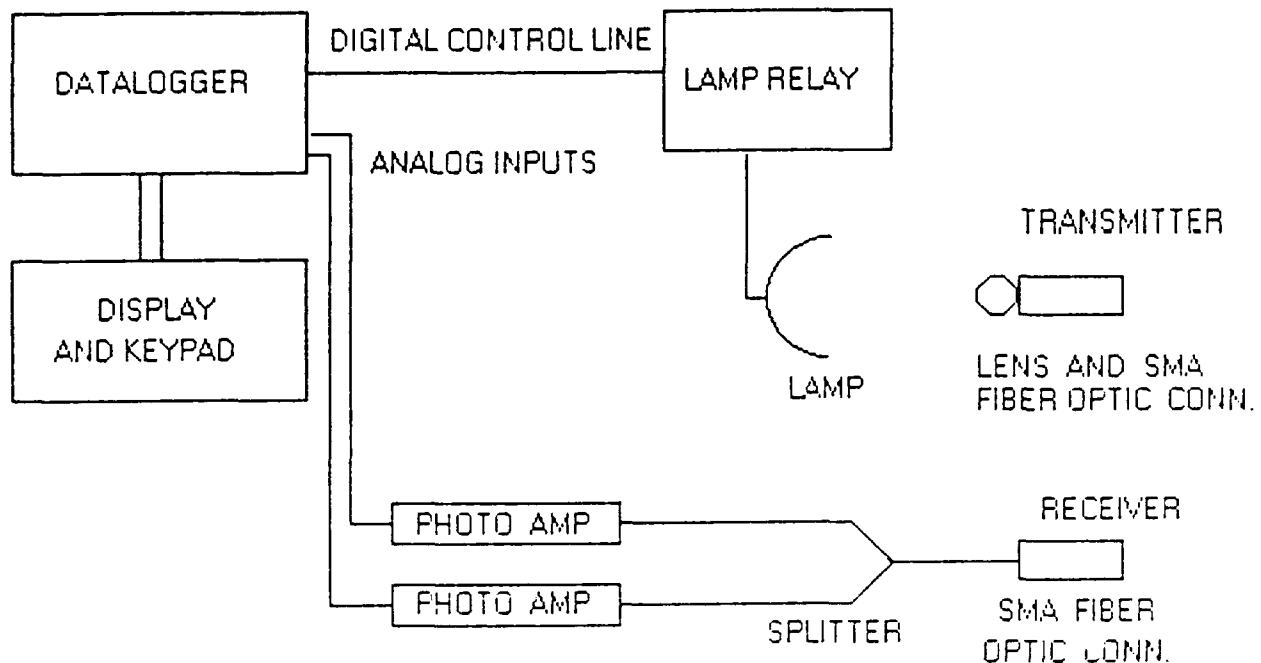


Figure 2. Block diagram of the instrument package.

This present system results in a package approximately 12 x 8 x 8 inches and weights about 10 pounds. Most of the weight is the gel cell and its charger. The datalogger and the photo-amplifiers are powered by a pair of 9 volt batteries while the lamp is powered by a 12 volt battery. The datalogger is programmed to take a background measurement of 200 readings from both amplifiers prior to the lamp being turned on. The lamp is then illuminated and the program pauses for 5 seconds, 200 readings are then taken and the lamp turned off. The datalogger then subtracts the background readings and ratios the signals. Since the 690 nm signal is unaffected by the TNT and the 520 nm signal is reduced, the ratio of 690nm to 520nm increases with TNT absorption.

3. SENSOR DESIGN

In a preliminary design (Zhang et. al. 1989) attached the membrane directly to a SMA connector and used a gold mesh or polished stainless steel as a mirror for a single fiber sensor system. In the current we use a GRIN ROD mounted on 200 um fiber optic cable and decided to use a dual fiber system as a transmission sensor (figure 3).

This sensor design gives much more sensor surface area than that of Zhang et. al. (1989) but does have the disadvantage of requiring a duplex fiber optic cable from the instrument to the sensor. The sintered stainless steel outer shell acts as a filter to keep particulate matter from



entering the optical path.

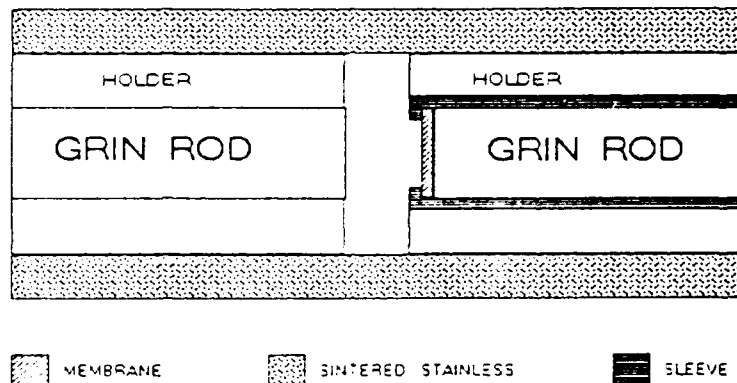


Figure 3. The sensor consists of two GRIN rods mounted on 200um fiber optic cable held within a sintered stainless steel tube by a pair of aluminum holders. The membrane is held in place by a sleeve over one of the rods.

4. EXPERIMENTAL DATA

As can be seen in figure 4 the real output of the 520nm signal decreases with time in the presence of TNT. The decrease amounts to about 40% after 6 hours in 2 ppm TNT. However, not all of the decrease is due to TNT since both 520 and 690 nm signals decreased with time in water but their ratio stayed constant.

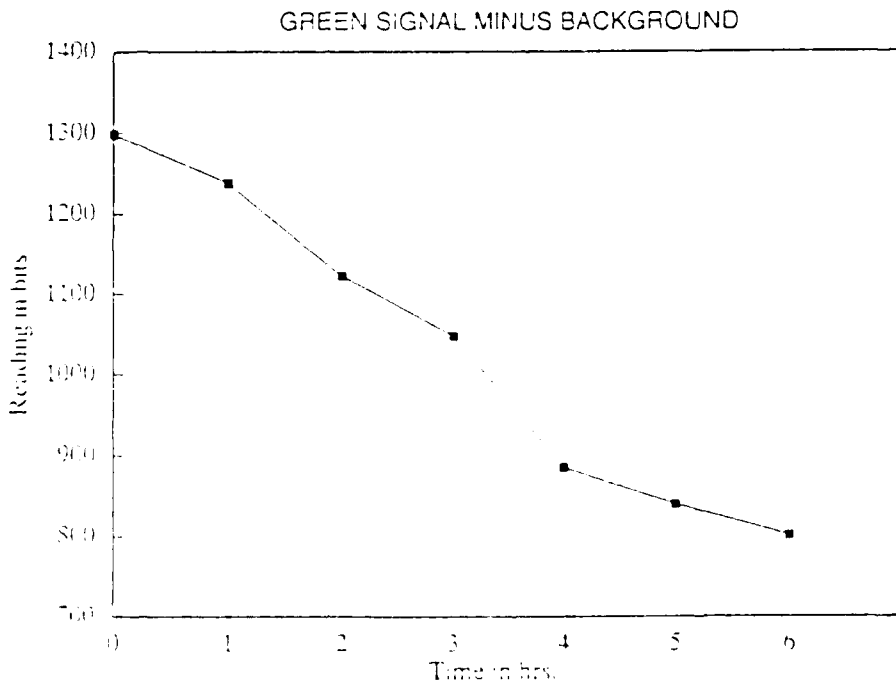


Figure 4.

Figure 5 shows the results of three different tests; one) no sensor in the system, just a fiber optic cable; two) Water only; and three) a solution of 2 ppm TNT. All tests were conducted with pieces cut from the same membrane.

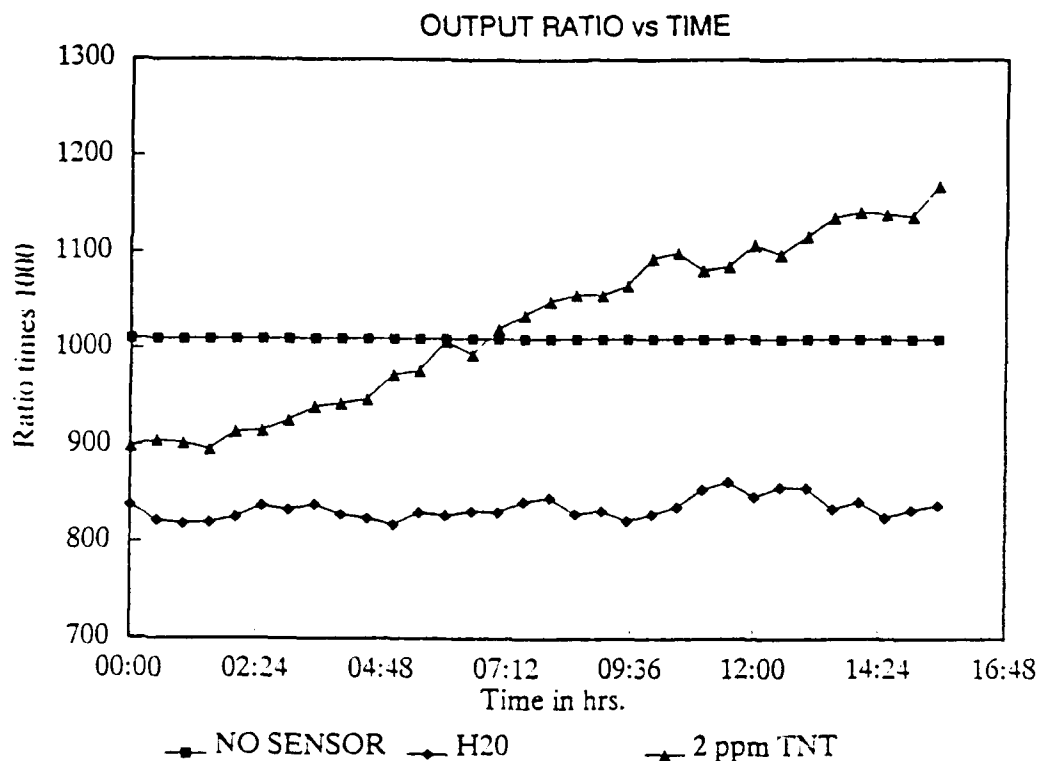


Figure 5.

5. CONCLUSIONS

Although preliminary tests show a response to TNT and the slope of the response is related to the quantity of TNT, this is far from a quantitative instrument.

Testing is continuing at the University of New Hampshire and will include comparison of different batches of membranes, detection limits and temperature testing. The latter being fairly important since all previous testing was done at room temperature. Finally field testing is yet to be done in locations with known TNT contamination.

6. REFERENCES

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ACKNOWLEDGMENTS

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A METHOD FOR COLLECTING SOIL SAMPLES BENEATH LAKE-BOTTOM SEDIMENTS

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ABSTRACT

Woodward-Clyde Federal Services (WCFS) is performing a Remedial Investigation/Feasibility Study (RI/FS) at the Cameron Station Military Reservation. Cameron Station, located in Alexandria, Virginia on 164 acres, has been identified for closure by 1995 pursuant to the Base Closure and Realignment Act of 1988.

Cameron Lake is a seven-acre surface water feature consisting of two interconnected ponds. The lake was formed in the 1950s by dredging soil and debris from a swampy area that had been used previously for waste disposal. Reports indicate materials such as wood, cardboard, and railroad ties and rails had been placed and burned at this location. Collection of soil samples beneath the lake was one aspect of the RI sampling program.

Initial plans called for mobilization of a barge-mounted drilling rig. The cost of this approach (over \$30,000) appeared excessive, however, for obtaining the six soil samples required by the Sampling Design Plan. An innovative method for obtaining soil samples from beneath the lake-bottom sediments without a drilling rig was devised. Manual soil sampling equipment customized with several attachments was used in conjunction with specially-fabricated casing to advance two soil borings into the native soil beneath the lake-bottom sediments. Access to the off-shore sampling locations, and an extremely stable working platform, was provided by rigidly connecting two small, flat-bottomed fishing boats.

This technique allowed the investigators to obtain discrete samples of soil from various depths in each soil boring while protecting the soil samples from possible cross-contamination by the lake sediments. The sampling objective was achieved at a fraction of the initially estimated cost.

1. INTRODUCTION

The Base Closure and Realignment Act of 1988 has resulted in the recommendation that over one hundred Defense Department facilities be closed or realigned. Cameron Station, located in Alexandria, Virginia on over 160 acres, has been identified for closure by 1995. Prior to disposing of the property, the environmental quality of the site must be evaluated.

Woodward-Clyde Federal Services (WCFS) is performing a Remedial Investigation/Feasibility Study (RI/FS) at Cameron Station for USATHAMA under contract DAAA15-90-D-0010. The objectives of the RI/FS are to define the nature and extent of any environmental contamination that may be present; assess the health and environmental risks associated with any such contamination; determine the necessity for remedial actions; and develop and evaluate remedial action alternatives.

An enhanced Preliminary Assessment (PA) of environmental contamination at Cameron Station was performed in 1989. That study found that the site did not represent an "imminent or substantial threat to the health of the surrounding populations or to the environment in general." Several potential areas of concern, however, were identified as requiring field investigation. Among the potential areas of concern was an on-site surface water feature known as Cameron Lake.



Today, the lake consists of the North and South Ponds, two relatively shallow (3 to 10 feet) ponds partially separated by a small island (Figure 1). It currently supports a large and diverse waterfowl population as it is located on a major migratory pathway. Historical information discovered in the PA indicated that in the late 1950s wood and possibly other materials had been burned at two "burn pits" whose locations corresponded to the present-day lake. Reportedly, the ashes and unburned material were removed from the burn pits after this waste management method was discontinued, and underlying soils and surrounding swampy area were excavated to form Cameron Lake.

It was uncertain whether any residual wastes, and associated soil and/or groundwater contamination resulting from disposal activities, were present at the old burn pits. Soil borings were planned at these locations, therefore, to allow collection of subsurface soil samples for detailed chemical analysis. The RI/FS Sampling Design Plan called for advancing two soil borings through the lake-bottom sediments, one at each of the burn pit locations, and collecting three underlying soil samples from each boring. The drilling subcontractor had proposed mobilizing a truck-mounted drilling rig and a barge, as well as ancillary and support equipment, to advance the borings. The estimated cost of this effort was approximately \$30,000. This seemed an excessive amount to recover a total of six soil samples, so WCFS devised a way to achieve the objectives of the Plan in a more cost-effective manner.

2. SAMPLING METHOD

The requirements for the lake boring method were to:

- Devise a stable working platform from which to advance the borings;
- Keep lake water and sediments from contacting the soil samples;
- Maintain an open borehole while retrieving the soil samples from successive sampling intervals; and
- Maintain sample integrity and minimize cross-contamination between sampling intervals.

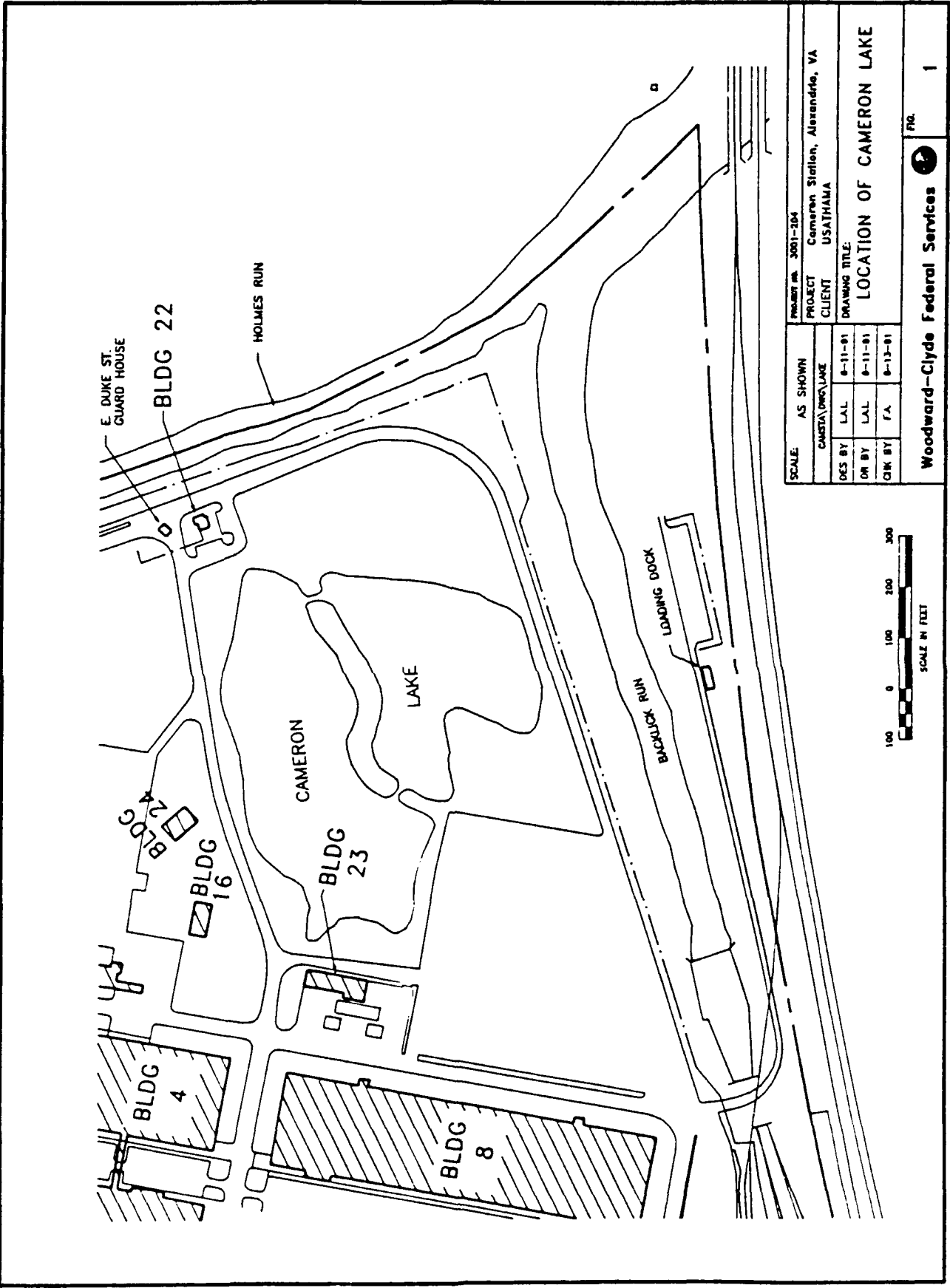
The basic elements of rotary drilling were combined with hand-augering techniques and readily available equipment to develop a method for advancing the boring through the soft, lake-bottom sediments and into the underlying soil. The first design requirement was initially thought to be met by construction of a raft. Concepts included a plywood platform on pontoons or air-tight drums. This evolved into a wooden (plywood or otherwise) platform over two fishing boats, which were readily available at the Cameron Station Recreation Center. As explained below, the platform concept evolved further into a much simpler method that came to light once the fishing boats were obtained. The remaining design requirements were satisfied using standard manual soil sampling equipment with specialized attachments, and specially fabricating casing material.

2.1 EQUIPMENT

The sampling equipment consisted of the following:

- Casing - Three-inch inside diameter aluminum irrigation pipe was cut into four-foot lengths, threaded on both ends and fit with couplings. One end of one of the sections of casing was machined into a "drive-shoe" configuration to serve as the lead casing.





SCALE: AS SHOWN		PROJECT NO. 3001-204
CAMERON LAKE		PROJECT Cameron Station, Alexandria, VA
DES BY LAL 8-11-81		CLIENT USATHAMA
DR BY LAL 8-11-81		DRAWING TITLE: LOCATION OF CAMERON LAKE
CHK BY F.A. 8-13-81		
Woodward-Clyde Federal Services		FIG. 1

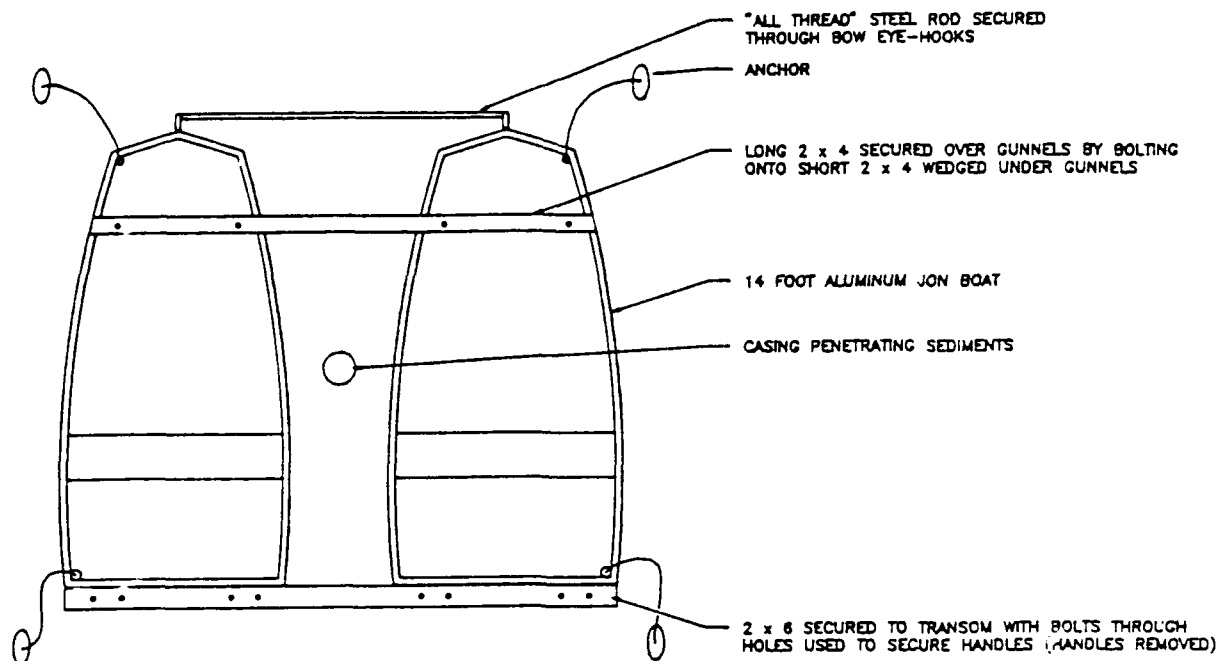
- **Soil Sampling Equipment** - Standard equipment used in manual soil sampling, along with some specialized attachments, met the design requirements. A 2.25 inch outside diameter soil recovery auger, mud auger, core soil sampler and sludge sampler were used. Interchangeable augering ends and core sampler ends with one-way butterfly valves were used depending on soil conditions. Stainless steel liners were used and changed between samples. A cross handle for rotating the auger or slide hammer for driving the core sampler were also used to advance the boring.
- **Other Equipment** - Other equipment included polyvinyl chloride (PVC) bailers, small hand tools, personnel protective equipment, and other supplies typically used in environmental sampling.
- **Work Platform** - Two 14-foot aluminum "jon" boats were borrowed from the Cameron Station Recreation Center for use in the lake sampling. The boats were fastened together using one 8-foot 2x4; two 2-foot 2x4s; one 8-foot 2x6; a 6-ft length of 3/8-inch "all thread" (essentially a very long bolt); and assorted washers, nuts and bolts. The 2x6 was fastened across the transom of each boat, utilizing the holes for the boat handles once they were removed. The all-thread conveniently fit through the bow eye-hooks. The small 2x4s were wedged under the gunnels towards the bow and the long 2x4 was bolted to the small ones. Figure 2 is a schematic diagram of the components described above. Figure 3 shows the platform deployed on the lake.

2.2 PROCEDURES

The sampling procedures followed standard practices commonly used in environmental investigations, as well as the applicable protocols and requirements of the USATHAMA Geotechnical Specifications. All equipment was steam-cleaned prior to use and between borings with approved water. Sampling equipment was also rinsed with deionized water. The following procedure was used to collect the soil samples:

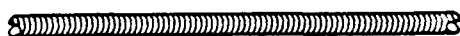
- One or more lengths of casing were attached to the lead casing with the couplings. Teflon tape was wound around the joints to ensure water-tight seals. The casing was pushed into the sediments as far as possible, and then hammered (using a small sledge-hammer and wooden block) to seat it into the underlying soil or stiff sediments.
- The lake water was bailed from within the casing and discarded overboard. The hand auger fit with the sludge sampler and butterfly-valve end was used to remove sediments from within the casing. Where the casing had not yet penetrated into the underlying soil, the casing was advanced as the sediments were removed until the underlying soil was encountered.
- The core sampler was fit with a fresh liner and sent down the boring for collection of the first sample. The sampler was driven through one foot of soil and then retrieved. Appropriate sample containers were filled with the recovered soil, labelled, and placed in a cooler.
- The next foot of soil was augered out to advance the boring to the next sampling interval. After the desired depth was reached, a fresh liner was inserted into the soil core sampler and the sample was collected as described above.
- These procedures were repeated to collect the additional samples.





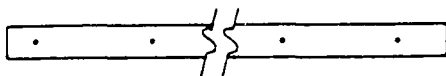
PLAN VIEW

MATERIALS



"ALL THREAD" STEEL ROD

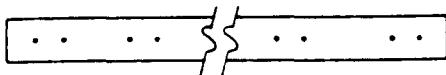
- 4 WASHERS
- 4 LOCK WASHERS
- 4 NUTS



LONG 2 x 4 WITH FOUR HOLES DRILLED



TWO SHORT 2 x 4'S WITH FOUR HOLES DRILLED FOR WEDGING UNDER GUNNELS



LONG 2 x 6 WITH EIGHT HOLES DRILLED FOR WEDGING UNDER GUNNELS

CLIENT USATHAMA

LOCATION Cameron Station, Alexandria, VA

Woodward-Clyde
Federal Services



TITLE SAMPLING PLATFORM

PROJECT NO. 3001-204

DESIGNED BY
CHECKED BY

LAL
F.A.

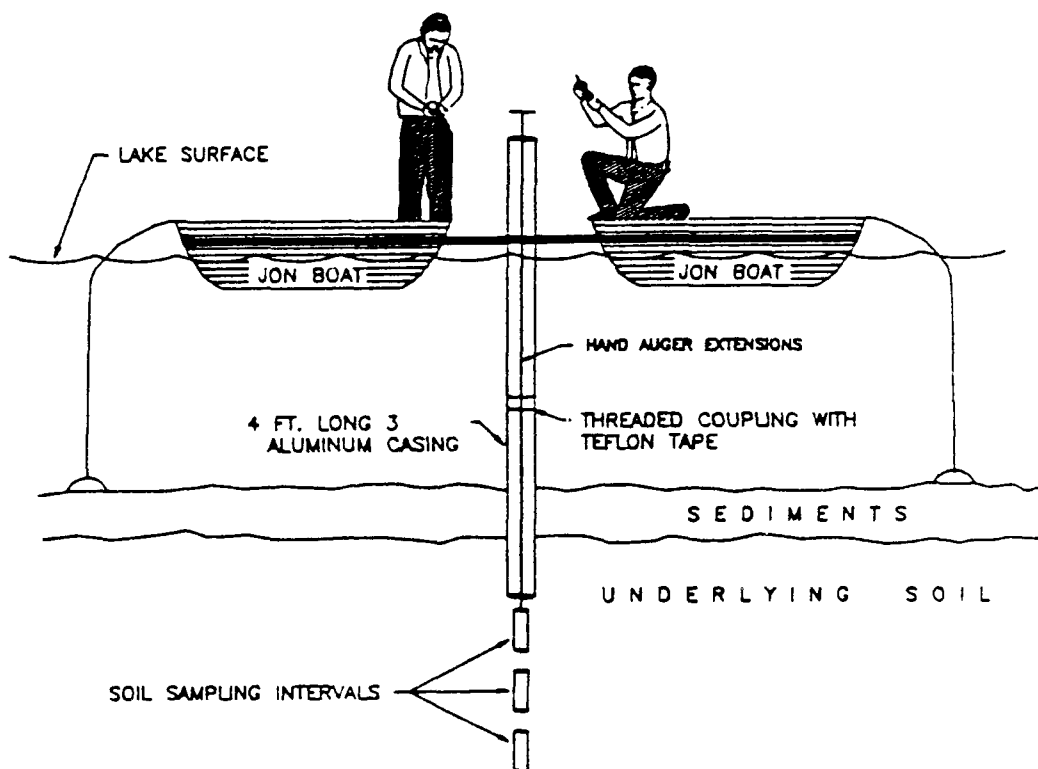
DATE
SCALE


8-11-91
N.T.S.

FIG.

2





CLIENT USATHAMA	LOCATION Cameron Station, Alexandria, VA				
Woodward-Clyde Federal Services 	TITLE SAMPLING METHOD				
	PROJECT NO. 3001-204	DRAWN BY CHECKED BY	L.A.L. P.A.	DATE SCALE	8-11-91 N.T.S.



- The casing was removed after collection of the last sample and the soft lake-bottom sediments collapsed into the borehole. [Grout was not used to avoid any potential adverse impacts to the aquatic environment or organisms.]

Figure 4 is a draft boring log for one of the lake borings, showing the details of the procedure

3. RESULTS

The sampling method proved very successful in allowing relatively undisturbed, intact and isolated samples of soil to be obtained from beneath the lake-bottom sediments. Both boats, all lumber, hardware and tools were easily transported to the lake in a small pickup truck. The platform provided an extremely stable platform from which to work. The platform was also very easy to maneuver in the water, requiring only the paddling normally required for a canoe or small fishing boat. The simplicity of the technique used to secure the two boats together allowed very quick mobilization and only minimal cost.

Some minor limitations were observed, although they probably can be overcome easily. The most important such limitations are summarized below.

- The limitations of manual soil sampling on land apply over water as well. Refusal due to cobbles or very dense soils may be encountered. This could probably be overcome by adding motorized hand-held augering equipment to the arsenal of supplies.
- In windy conditions, additional anchoring capacity may be required. The two-man crew standing up working on the platform acted as a sail that caught enough wind on one occasion to cause the platform to drift away from the boring. Four anchors are recommended, one off each corner of the platform. Additional measures to prevent drifting, such as tethering the platform to an upwind tree or other stationary point, could address this problem also.
- Advancing the borings in granular soils generally will require advancing the casing as successive samples are retrieved. A means to spin-and-drive the casing in such cases should be available if such soils are expected to be encountered.
- Retrieving a sample that has been collected by driving the soil core sampler using the slide hammer can be difficult. An alternative approach in dense soils is advancing the core sampler fit with an augering end by turning the cross handle instead of driving it.

4. ACKNOWLEDGMENTS

The authors wish to thank Jim and Rick of Art's Manufacturing and Supply, American Falls, Idaho for their help in selecting the equipment; Dennis Bowser (Project Geologist) and Kristine Kingery (Project Officer) of USATHAMA for considering an alternative approach to a problem, and Charles Brummett of Cameron Station (EACA, USACE) for arranging our use of the boats and other logistical support.



DRAFT BORING LOG

PROJECT NAME: Cameron Station

LOCATION: Alexandria, VA

DRILLING METHOD: 3" casing/hand

DATE COMPLETED: 03/04/90 auger

SURFACE ELEVATION: Lake Surface

PROJ. NO. 3001

WATER DEPTH: N/A

During Drilling — ft.

After — hr, — ft.

After — hr, — ft.

Boring CL-7

Sheet 1 of 1

DEPTH (ft)	NO.	SAMPLE REC	RES	DESCRIPTION	DESCRIPTION OF BORING AND SAMPLING PROCEDURES
0				Lake Surface	1. Pushed casing —
1					through sediments —
2					& hammered to seal. —
3				Water	2. Bailed water —
4					from inside casing. —
5					3. Removed sediments —
6					from casing with —
7					hand auger and sludge —
8					sampling attach- —
9					ment. —
10	S-1	12'	N/A		4. Drove sampler —
11					through first 1' of —
12	S-2	12'	N/A		soil and collected —
13					sample S-1. —
14	S-3	12'	N/A		5. Augered next 1' —
15					of soil & discarded. —
16					6. Hand augered —
17					next 1' of soil and —
18					collected sample S-2 —
19					7. Hand augered next —
20					1' of soil and —
21					discarded. —
22					8. Hand augered —

NOTES:

1. Hand augered soil material between sample intervals.
2. Borehole collapsed upon removal of casing.
3. Bottom of boring at 14 ft. below lake surface.

adon USATHAMA

Woodward-Clyde
Federal Services

Hazardous Waste Minimization and VOC Reduction at U.S. Army Depots:
USATHAMA R&D Efforts

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ABSTRACT

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is conducting research and development projects pertaining to minimization of hazardous waste and reduction of volatile organic compound (VOC) emissions generated during depot operations. Under contract with USATHAMA, IT Environmental Programs, Inc. (formerly PEI Associates, Inc.), recently assisted in the evaluation of several commercially available technologies for their waste minimization and VOC reduction potential.

One project evaluated under this contract involved the purification and rejuvenation of chromic acid solutions by electrodialysis at Corpus Christi Army Depot (CCAD), Texas. USATHAMA purchased a full-scale, 500-amp electrodialysis system and installed it on a chromic acid stripping solution and a hard-chromium electroplating bath. The system was tested and evaluated for its ability to remove contaminant metals and to oxidize trivalent to hexavalent chromium as a means of increasing bath life and quality and reducing hazardous waste.

A second project involved evaluating the use of a filtration system to extend the life of an alkaline-based paint stripper at Letterkenny Army Depot (LEAD) in Chambersburg, Pennsylvania. The objective of this test was to remove particulates from the process bath, to increase bath life, to lower the frequency of tank changes, and to effect an overall reduction in hazardous waste.

A third project entailed the evaluation of high-volume, low-pressure (HVLP) paint spray guns at Sacramento Army Depot (SAAD), California. Three commercially available spray guns were purchased and evaluated for the maximum transfer efficiencies attainable on parts routinely processed. Higher transfer efficiencies would lower VOC emissions by reducing the quantity of paint used, and could decrease the amount of hazardous waste by reducing the amount of paint overspray captured in air pollution control devices.

This paper presents the results of these three projects.

* Originally presented at the 15th Annual Army Environmental R&D Symposium, June 25 - 27, 1991, Williamsburg, Virginia, sponsored by USATHAMA.



INTRODUCTION

U.S. Army depots throughout the country maintain, repair, and overhaul a wide variety of military equipment, including tanks and other vehicles, engine components, electronic communication shelters, and helicopters. Typical operations include metal preparation (cleaning, degreasing, and removal of paint and other surface coatings) and metal finishing (electroplating, conversion coating, and paint application) processes. Large quantities of hazardous waste, wastewater discharges, and air emissions are generated during these operations.

As part of its commitment to environmental compliance, the U.S. Army has established a goal of 50 percent reduction of hazardous waste by 1992 relative to 1985 baseline figures. The Depot Systems Command (DESCOM) has targeted six waste streams for major reductions at Army depots: petroleum-based solvents, Industrial Waste Treatment Plant sludges, metal conversion coatings, chemical paint stripping, chlorinated solvents, and metal plating.

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is currently conducting research and development projects to assist depots in meeting their waste minimization goals. As part of this effort, USATHAMA and its contractor, IT Environmental Programs, Inc. (formerly PEI Associates, Inc.), conducted visits to eight Army depots: Anniston (Alabama), Corpus Christi (Texas), Letterkenny (Pennsylvania), Red River (Texas), Sacramento (California), Sharpe (California), Tobyhanna (Pennsylvania), and Toole (Utah) Army Depots. The objective of these visits was to identify waste minimization practices and opportunities for research and development (R&D) projects related to waste and volatile organic compound (VOC) reduction.

These depot visits resulted in the selection of three commercially available technologies for full-scale implementation at Army depots to reduce hazardous waste and VOC emissions from surface preparation/finishing operations:

- Chromic Acid Purification/Recovery by Electrodialysis at Corpus Christi Army Depot.
- Particulate Filtration of Alkaline Paint Stripper at Letterkenny Army Depot.
- Evaluation of high-volume, low-pressure (HVLP) paint application systems at Sacramento Army Depot.

Each of these USATHAMA R&D efforts and the results achieved to date are discussed in this paper.



CHROMIC ACID PURIFICATION/RECOVERY BY ELECTRODIALYSIS AT CORPUS CHRISTI ARMY DEPOT

Chromic acid solutions are widely used at various Army depots for chromium electroplating, chromate conversion coatings, removal of chromate conversion coatings (chromic acid stripping), and anodizing. After a period of use, these solutions become contaminated with metals that are introduced into the system by drag-in from other tanks or by dissolution of metals that compose the parts, tanks, tank liners, anodes, or bus bars. In addition, hexavalent chromium (the form of chromium that constitutes chromic acid) is reduced to trivalent chromium, which is an impurity. In chromic acid stripping solutions, the buildup of contaminants may reduce the removal rate of the conversion coating. In plating baths, a buildup of contaminants may cause plating quality problems such as differences in roughness, and may also cause a loss of plating efficiency. Hazardous wastes are generated by the following: disposal of spent solutions when the contamination builds up excessively, disposal of sludge buildup in the plating bath due to precipitated metal salts, reprocessing of parts rejected because of plating quality problems, and the treatment of rinse water containing heavy metals. Reducing the contamination in these process solutions could result in hazardous waste reduction.

For this project, USATHAMA purchased a full-scale, 500-amp electrodialysis system and installed it on two tanks at Corpus Christi Army Depot (CCAD). Together, USATHAMA and IT then conducted a test program to determine the advantages and disadvantages of this type of technology. Figure 1 is a diagram of an electrodialysis cell in which voltage is applied to drive positive ions through a cation-permeable membrane. The anode and cathode are surrounded by the process solution (anolyte) and a catholyte solution, respectively. As the contaminant metal ions pass through the semipermeable membrane, they react with hydroxide ions formed at the cathode and precipitate out of solution. At the anode, hydrogen ions are formed and trivalent chromium is partially oxidized to hexavalent chromium, which exists as the negative chromate ion and does not pass through the membrane. Some trivalent chromium may be transported through the membrane rather than being oxidized. The hydrogen and chromate ions form a solution of chromic acid that can be returned to the process bath. The process tank can thus be continuously purified, which extends the life of the solution and improves the solution quality. Alternatively, a spent chromic acid solution could be recovered by removing the contaminant metals. The purchased equipment is designed so that the anode fits directly inside the process tank. A diagram of the electrodialysis unit is shown in Figure 2.

Chromic-Acid Stripping Solution

During the first phase of testing, the electrodialysis equipment was installed on a 269-gallon holding tank of chromic acid solution that had been used for removing chromate conversion coatings from magnesium parts (see photo, Figure 3). This



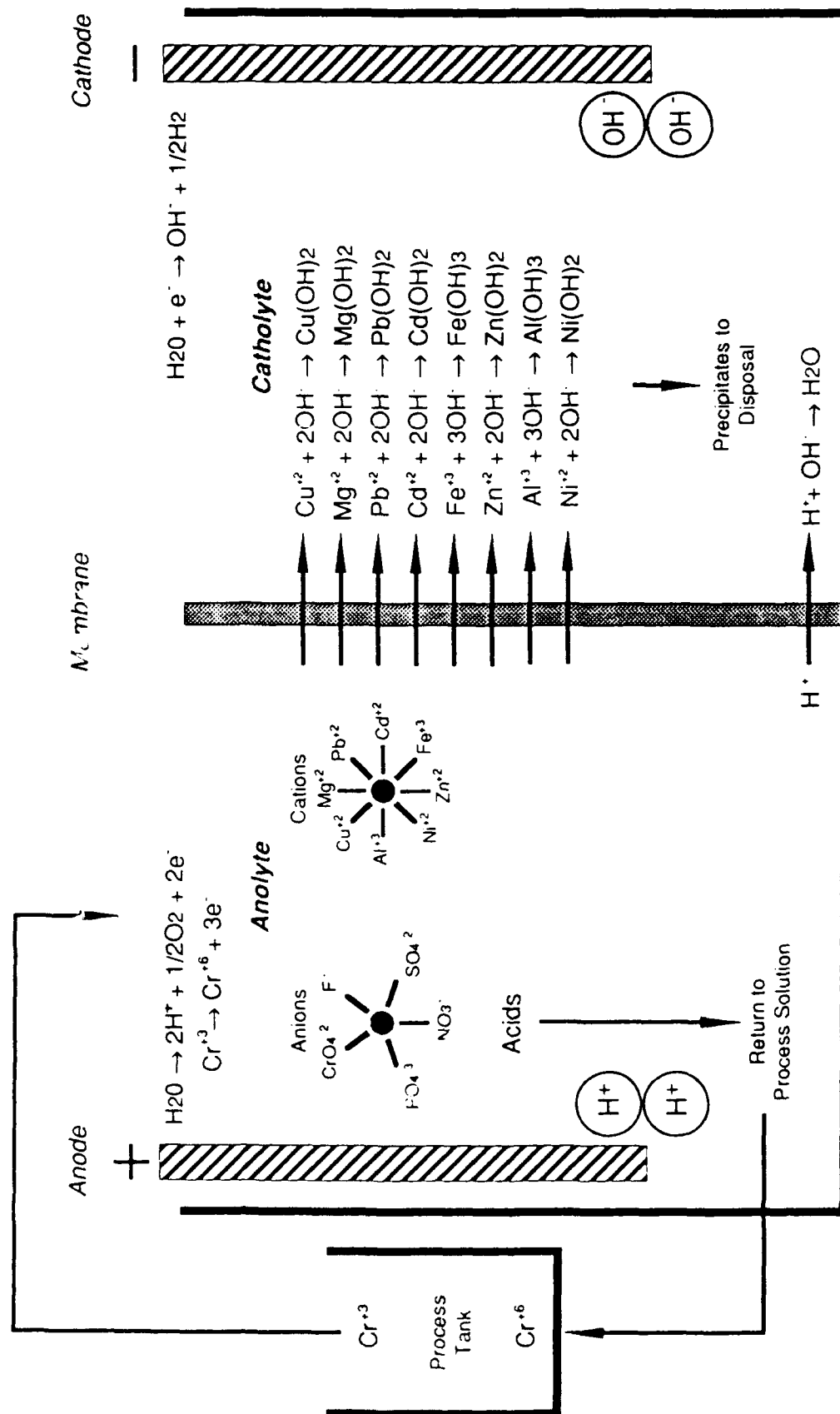
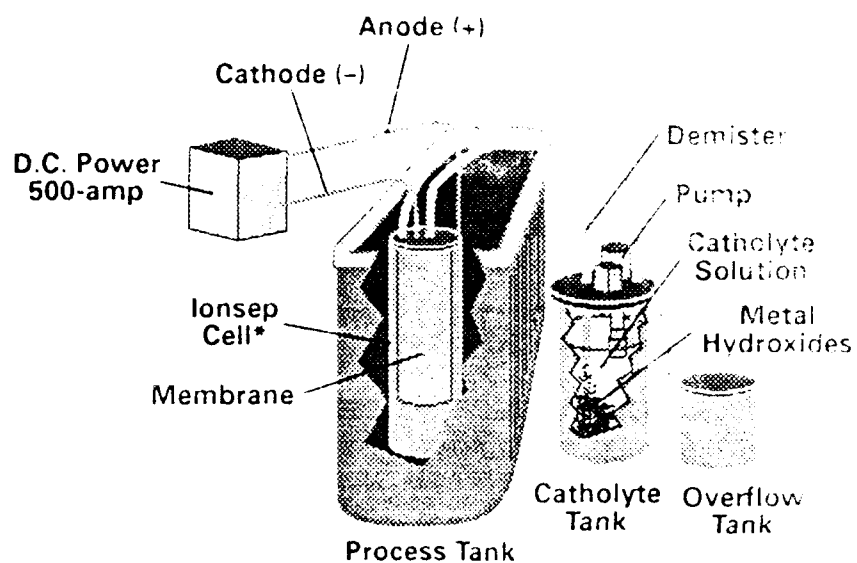


Figure 1. Schematic of two-compartment electroplating cell.



*Ionsep Electrochemical Cell manufactured under U.S. Patent No. 4,654,137

Figure 2. Ionsep Electrochemical Cell

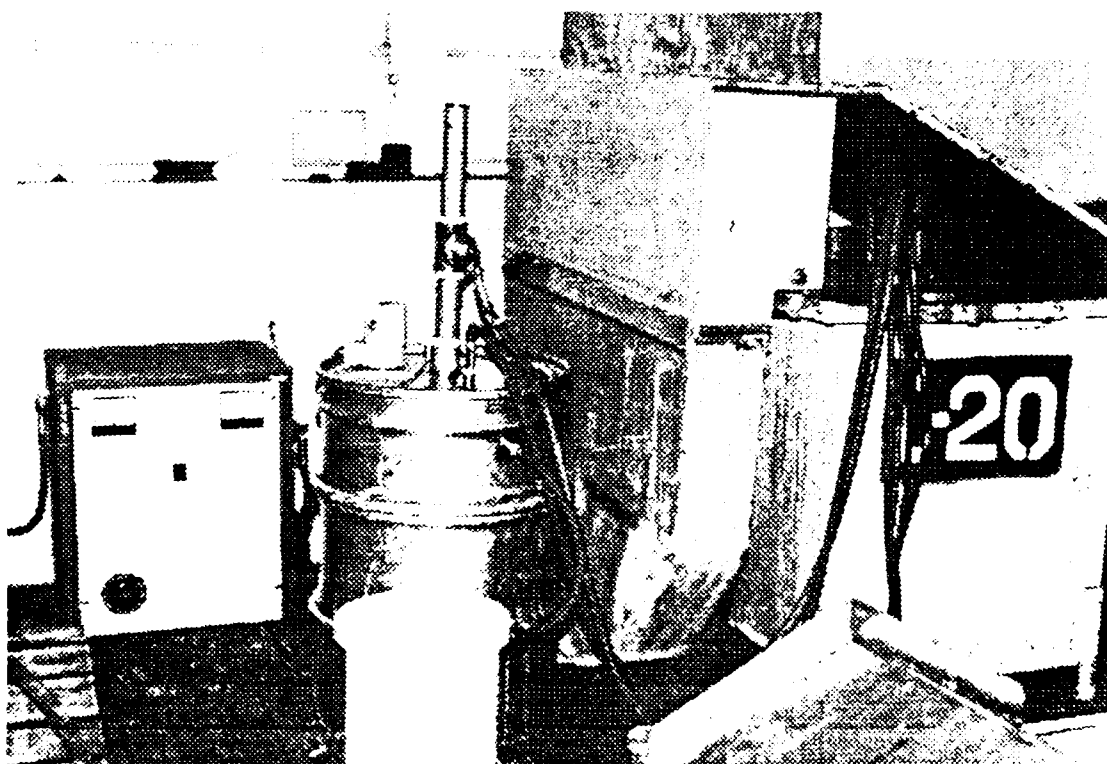


Figure 3. Electrodesalination cell installed on chromic acid stripping solution



solution had become spent after several weeks of use and was stored in a holding tank. The objective of the testing was to regenerate the solution for reuse by removing contaminant metal ions and by oxidizing trivalent to hexavalent chromium. During the testing, the unit was operated for 593 hours and 205,000 amp-hours over a period of 44 days. The equipment was shut down for a total of 138 hours over the 44 days for the following reasons: normal weekend shutdowns, changing the catholyte, replacing a leaking membrane, and other maintenance and repair functions not directly related to operation of the electrodialysis unit.

After 2 weeks of testing, CCAD personnel determined that the catholyte was leaking into the process solution through a puncture in the membrane. The membrane was replaced by the vendor and testing was continued. (The consequences of this leak are discussed later.)

Table 1 presents the concentration data for the four primary metal contaminants studied during this phase of the project - aluminum, iron, magnesium, and zinc. Table 2 presents data for other metals (barium, cadmium, calcium, cobalt, manganese, and silicon) detected in the process solution during the test program either before and after the membrane leak or at the beginning and end of the test period. Figure 4 is a graph of the metal concentrations detected during operation of the electrodialysis cell; metals other than the four primary contaminants are shown as a total.

As expected, the concentration of metals decreased with increasing amp-hours, which indicates that the metals were transported across the membrane into the catholyte solution. Over the period of testing, 60.3 percent of the major metal contaminants were removed, including 79.0 percent of the aluminum, 45.6 percent of the iron, 76.9 percent of the magnesium, and 72.3 percent of the zinc. A total of 51.7 percent of the other detectable multivalent metals were also removed. Both the data and graph show that the efficiency of the electrodialysis process decreases with decreasing metal concentration: 72 percent of the metals removed during testing were removed during the first 47 percent of the amp-hours.

Table 2 indicates that the concentration of sodium increased from a low of 179 mg/L to 2,840 mg/L after the membrane leak was noticed. This increase in concentration resulted from sodium sulfate and sodium carbonate leaking from the catholyte into the process solution. Figure 4 shows a slight increase in metal concentrations between the samples analyzed before and those analyzed after the membrane leak. Some of the metals removed during the electrodialysis were apparently transported back into the solution through the membrane leak.

In addition to the removal of metal contaminants, the other criterion for evaluating the success of the electrodialysis unit was oxidation of the trivalent chromium to hexavalent chromium. All samples were initially analyzed for total and hexavalent chromium, and trivalent chromium was determined by the difference. In

TABLE 1. CONCENTRATIONS OF PRIMARY METAL CONTAMINANTS IN CHROMIC ACID STRIPPING SOLUTION (mg/L)

Contaminant	Amp-hours							Reduction by 97,000 amp-h, %	Overall reduction, %
	0	1,900	7,100	14,300	32,300	51,300	97,000	205,000 ^a	
Aluminum	649	598	564	519	443	383	267	136	58.9
Iron	4410	4070	3910	3830	3610	3390	2990	2400	32.2
Magnesium	3270	3020	2760	2630	2240	1950	1410	756	56.9
Zinc	<4 ^b	61.3	59.6	55.5	46.2	42.0	30.2	17.0	50.7 ^c
Total	8329	7749	7294	7034	6339	5765	4697	3309	43.6
									60.3

^a This was the first sample taken after the membrane leak was noticed.

^b Not detected. The concentration shown is the detection limit for the analyte.

^c Calculated from the 1900-amp-h sample.

TABLE 2. CONCENTRATIONS OF NONCRITICAL METALS IN CHROMIC ACID STRIPPING SOLUTION (mg/L)

Contaminant	Amp-hours				Reduction by 97,000 amp-hours, %	Overall ^b reduction, %
	0	97,000	106,000 ^a	205,000		
Multivalent metals ^c						
Barium	10.8	-	-	2.2	-	79.6
Cadmium	63.4	28.4	30.4	15.7	55.2	75.2
Calcium	85.7	32.2	34.0	13.2	62.4	84.6
Cobalt	14.6	-	-	31.5	-	-116
Manganese	104	48.4	53.7	29.4	53.5	71.7
Silicon	50.2	-	-	66.9	-	-33.3
Total	329	-	-	159	-	51.7
Monovalent metals						
Potassium	4150	-	-	4080	-	1.7
Sodium	179	1790	2840	1530	-900	-755

^a This was the first sample taken after the membrane leak was noticed.

^b A negative number indicates an increase in concentration.

^c Other metals analyzed for but not detected were antimony, beryllium, lead, nickel, silver, thallium, thorium, and vanadium.

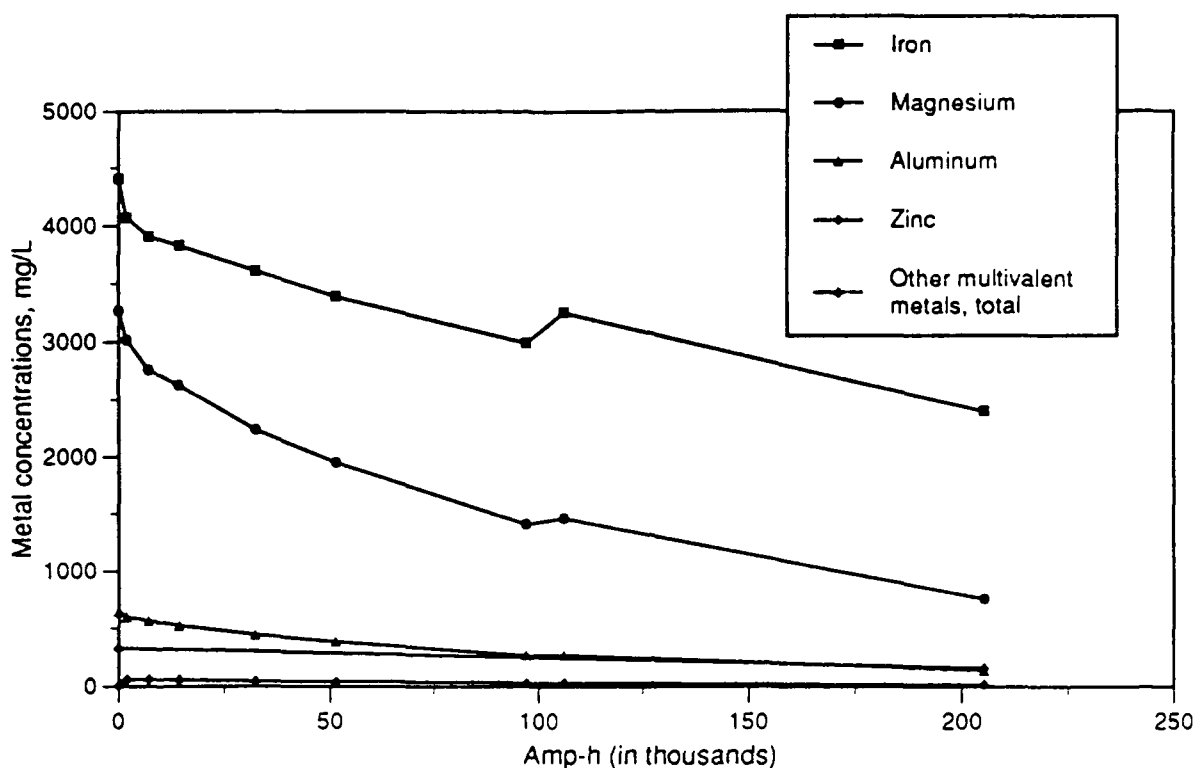


Figure 4. Concentration data for major metal contaminants in chromic acid stripping solution.

these particular process samples, however, the concentrations of total and hexavalent chromium were very high (greater than 100,000 mg/L), and the trivalent chromium concentration was much lower (less than 10,000 mg/L). The analytical uncertainty of the total and hexavalent chromium concentrations was greater than the total concentration of trivalent chromium, and sometimes the analytical result for hexavalent chromium was higher than that for total chromium because of the analytical uncertainty. Therefore, the concentration of trivalent chromium could not be determined by difference. The visual evidence obtained indicated a reduction in trivalent chromium concentrations despite the fact this reduction could not be quantified analytically. During the test program, the appearance of the solution turned from the black color of a solution contaminated with trivalent chromium to the bright red of a fresh solution. The reduction in trivalent chromium concentrations may have been due to the migration of trivalent chromium through the membrane, the oxidation of trivalent to hexavalent chromium, or, most likely, a combination of both.

As mentioned previously, the contaminant metals are precipitated in a catholyte solution contained in a 55-gallon drum. This catholyte occasionally becomes spent

and must be disposed of as waste generated by the electrodialysis process. During this phase of the test program, the catholyte was changed six times. The first spent catholyte consisted of approximately 47 percent sludge, of which 78 percent was moisture. Table 3 presents the characteristics of the spent catholyte sludge and liquid. The chromium and cadmium concentrations in the sludge would probably necessitate disposal of the sludge as a hazardous waste. The liquid fraction would require treatment for hexavalent chromium and neutralization before its disposal.

Membrane Leak

The ultimate goal of this first phase of testing on the chromic acid stripping solution was to use the rejuvenated solution in the actual processing line and to operate the electrodialysis cell in the process solution on a continuous basis. At the end of the batch rejuvenation, the solution was pumped to the process line, heated to the operating temperature, and used to process parts. The solution appeared to be successful in removing the chromate conversion coating. After a few parts were processed, however, the solution was found to be etching the magnesium parts because of the sulfates that had leaked into the process solution through the hole in the membrane (the catholyte consists largely of sodium carbonate and sodium sulfate). The analytical result for total sulfates was 2,220 mg/L. The sulfates and chromic acid are believed to have formed a pickling solution that chemically attacked the magnesium parts. The membrane was replaced, but a very small leak was discovered in the new membrane.

Following the first test phase, a laboratory test was devised to treat the sulfate-contaminated solution with barium carbonate to precipitate the sulfates; the carbonate forms carbon dioxide gas and leaves the solution. Magnesium strips were used to test the etching rate of the solution before and after treatment with barium carbonate. A fresh solution of chromic acid was used as a control. The results are presented in Table 4. A magnesium strip lost 79.0 percent of its weight when heated at boiling for 90 minutes in the chromic acid solution contaminated with sulfates. After treatment with an excess of barium carbonate, another magnesium strip lost only 2.71 percent of its weight compared with a 1.44 percent weight loss when immersed in the chromic acid solution used as a control. The concentration of sulfate was reduced from 2,220 mg/L in the contaminated solution to 970 mg/L in the sample treated with barium carbonate (compared with 750 mg/L sulfate in the fresh chromic acid solution).

These results show that the use of the electrodialysis unit could contribute sulfates to the process solution in the event of a membrane leak, which could result in parts damage and render the solution effectively useless. The electrodialysis unit with this catholyte formulation should not be used in-line on a solution in which sulfate contamination would negatively affect its operation. The lab results, however, indicate that the solution can be successfully rejuvenated by the addition of barium carbonate in the event of sulfate contamination. Therefore, spent chromic acid solutions could



TABLE 3. CHARACTERISTICS OF CATHOLYTE SAMPLES FROM CHROMIC ACID STRIPPING

Matrix	Fresh catholyte, mg/L	Sludge, mg/kg	Filtrate, mg/L
Primary contaminants			
Aluminum	<13 ^a	2,400	122
Iron	9.48	9,450	2.14
Magnesium	8.16	14,700	3.57
Zinc	<4	268	<0.2
Total chromium	NA ^b	3970 (mixed sludge/liquid)	
Hexavalent chromium	NA	250	106
Other metals ^c			
Barium	0.099	7.92	<0.02
Cadmium	<1	254	<0.05
Calcium	75.8	507	0.242
Cobalt	<10	20.9	<0.4
Manganese	0.38	406	0.074
Nickel	0.544	48.2	<0.4
Weight percent	-	47	53
Moisture content of sludge, %	-	78	-

^a Not detected. Concentration shown is the detection limit for the analyte.

^b NA = Not analyzed.

^c Other metals analyzed for but not detected were beryllium and silver.

TABLE 4. RESULTS OF ETCHING RATE TESTING

Description of sample	Sulfate concentration, mg/L	Weight lost to etching, %
New chromic acid solution (control)	750	1.44
Spent chromic acid solution after treatment by electrodialysis	3000	79.0
Spent chromic acid solution after treatment by electrodialysis and BaCO ₃	970	2.71



be batch-treated by electrodialysis in a holding tank, analyzed for sulfates, treated with barium carbonate, and then pumped back to the in-line operating tank through a filter for removal of the barium sulfate sludge.

Chromium Plating

After the first test phase on the chromic acid stripping solution, the electrodialysis equipment was installed on a hard chromium electroplating bath. Chromium plating baths typically contain sulfates as part of the solution formulation, which means a membrane leak would likely be less critical. The direct objective of the testing was to remove metal contaminants and to oxidize trivalent chromium to hexavalent chromium. The ultimate desired benefits of this approach were to extend the life of the plating solution, to maintain or increase the plating efficiency, to reduce sludge buildup in the tank as a result of the precipitation of metal salts, and to reduce the number of parts rejected as a result of the metal contaminants interfering with plating quality.

During this second phase of testing, the electrodialysis unit was installed on a 456-gallon-capacity chromium-plating tank. The equipment was operated for a total of 1,031 hours and 331,000 amp-hours over 90 days. The equipment was shut down for 1,129 hours for normal weekend shutdowns, for catholyte changes, and for other functions not directly related to the operation of the electrodialysis unit.

Tables 5 and 6 summarize the analytical data for the contaminant metals in the chromium-plating tank. Table 5 presents the concentrations of primary metal contaminants (copper, iron, and nickel), and Table 6 presents the concentrations of noncritical metals. These data indicate overall removal rates of 73 percent of the copper, 62 percent of the iron, and 59 percent of the nickel. An average 44 percent reduction was achieved for all other multivalent metals that were analyzed. A graph of the metal concentrations over time is provided in Figure 5.

In the first phase of testing on the chromic acid stripping solution, the concentration of trivalent chromium could not be determined by the analytical method used. During the second test phase, a miniature cell similar to the full-scale unit was used to determine the trivalent concentration. The minicell was fitted with a nonoxidizing anode to prevent oxidation of the trivalent chromium. During operation of the cell, metal ions, including copper and trivalent chromium, are transported across the membrane and precipitate in the catholyte. Because hexavalent chromium is not transported across the membrane, all the chromium in the catholyte sludge is in the trivalent form and the sludge can be analyzed for total chromium to obtain the trivalent chromium concentration. It is assumed that the ratio of trivalent chromium to copper in the sludge is the same as the ratio in the process solution. Therefore, measuring the concentrations of total chromium and copper in the sludge and copper in the



TABLE 5. CONCENTRATIONS OF PRIMARY METAL CONTAMINANTS
IN CHROMIUM PLATING SOLUTION
(mg/L)

Contaminants	Amp-hours						Reduction by 156,000 amp-h, %	Overall reduc- tion, %
	0	13,800	60,800	156,000	260,000	331,000		
Copper	145	144	136	131	47	39	9.7	73
Iron	475	466	456	393	200	180	17.3	62
Nickel	13.7	15.3	14.3	12.4	7.2	5.6	9.5	59
Total	634	626	606	536	254	225	15	65
Trivalent chromium	2120	1678	-	-	364	-	-	-

TABLE 6. CONCENTRATIONS OF NONCRITICAL METAL CONTAMINANTS
IN CHROMIUM PLATING SOLUTION
(mg/L)

Contaminant	Amp-hours			Overall reduction, %
	0	260,000	331,000	
Multivalent ^a				
Aluminum	34.2	10	7.5	78
Antimony	<0.09 ^b	2.0	2.4	-
Barium	0.593	0.3	0.25	58
Cadmium	5.51	2.6	2.0	64
Calcium	36	7.1	4.6	87
Cobalt	28.7	20	20	30
Lead	<0.2	5.6	18	-
Magnesium	8.56	1.5	0.94	89
Manganese	3.61	1.5	1.2	67
Silicon	16.7	<2	<2	>88
Thallium	<0.3	12 ^c	22 ^c	-
Vanadium	<0.008	1.4	1.4	-
Zinc	14.7	4.2	3.5	76
Total	149	68.2	83.8	44
Monovalent				
Potassium	7000	6200	6500	7.1
Sodium	185	220	280	-51

^a Other metals analyzed for but not detected were beryllium and silver.

^b Not detected. The concentration shown is the detection limit for the analyte.

^c Detection limit = 12 mg/L.

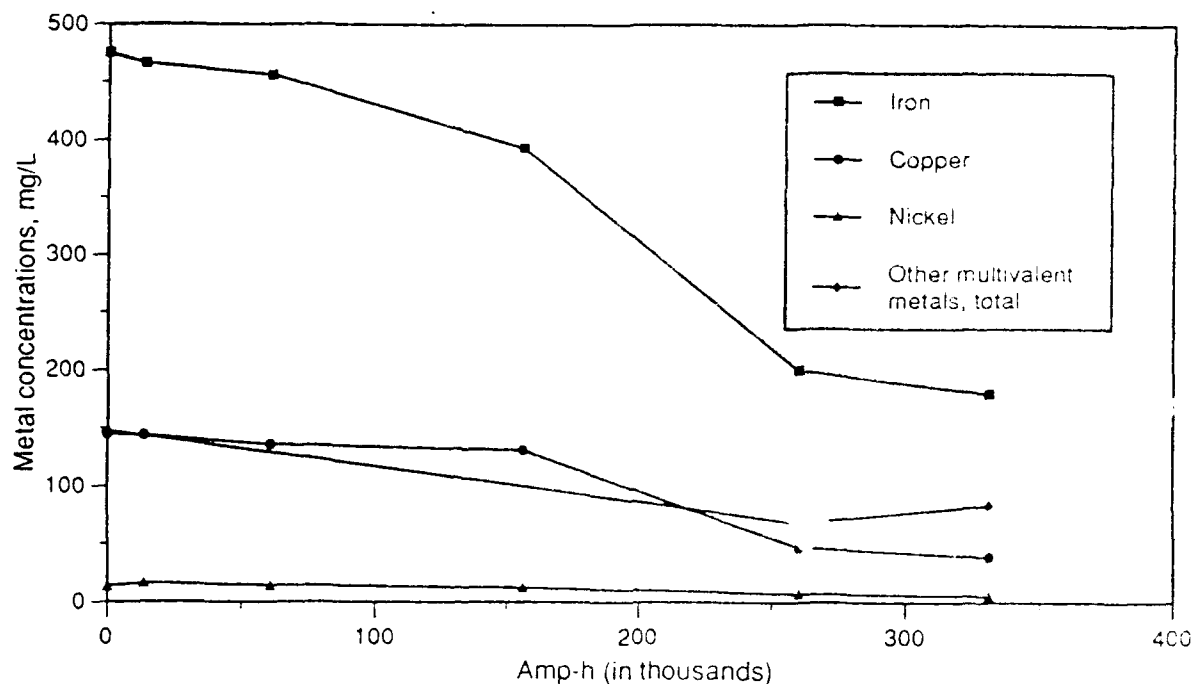


Figure 5. Concentration data for metal contaminants in chromium plating solution.

process solution permits calculation of the concentration of trivalent chromium in the process solution.

Table 5 presents the calculated trivalent chromium concentrations in the chromium-plating solutions. After 260,000 amp-hours (approximately 79 percent of the total test program), the concentration of trivalent chromium was reduced from 2,120 to 364 mg/L, an 83 percent reduction. These results are further confirmed by the fact that the appearance of the solution turned from the black color of a solution contaminated with trivalent chromium to the bright red of a fresh chromic acid solution.

Electrodialysis was successful in significantly reducing contaminant metal and trivalent chromium concentrations in the chromium-plating solution. Sufficient data were not collected, however, to verify the desired ultimate benefits of the system, which are reduction of hazardous waste, reduction of part rejects, reduction in sludge buildup, and increase in plating efficiency. Longer-term monitoring of the system is needed to measure the magnitude of these problems and to verify the benefits of operating the electrodialysis unit. The system would also be more useful on a tank that is subjected to heavier usage and is more contaminated. Finally, in a closed-loop system, in which contaminant metals become more concentrated because they are recovered from the rinse water and returned to the process solution, the electrodialysis

unit would be useful in maintaining a clean bath. If ion exchange is used to recover chromium from rinse water (which greatly reduces waste because sludge is not generated by wastewater treatment) electrodialysis can be used to recover the regenerant solutions.

Catholyte Characteristics

During the chromium plating test program, the catholyte was changed two or three times, which generated 100 to 150 gallons of hazardous waste and wastewater. The generation of sludge was much lower than during the test program on the chromic acid stripping solution because the plating solution was less contaminated, and each catholyte solution lasted a month or more. Table 7 presents the concentrations of contaminant metals in the catholyte sludge and liquid. When these samples were collected, only a small amount of sludge had formed. Analysis showed the sludge contained up to 158,000 mg/kg of chromium.

As previously mentioned, hexavalent chromium concentrations in the catholyte solution could present a treatment and disposal problem. Two methods were tested to reduce the hexavalent to trivalent chromium in the catholyte drum itself. In one method, the sodium metabisulfite concentration in the catholyte was doubled, and the cell was allowed to run so that the reducing potential of the cathode in combination with the sodium metabisulfite would reduce the hexavalent chromium. This method resulted in an 87 percent reduction of hexavalent chromium concentration, from 35 to 4.5 mg/L. In another method, a sample of catholyte was treated with a small amount of a proprietary alkaline reducing agent. This method reduced the hexavalent chromium concentration by 60 percent, from 810 to 320 mg/L. It should be noted that the chemical dosages were not optimized in either case, and these results should not be compared directly. Increasing the dose of either agent would probably result in greater reductions in hexavalent chromium.

Potential Problems and Solutions

Potential disadvantages of the operation of the electrodialysis system include membrane leakage (especially of sulfates into a solution in which they can damage parts), the volume of catholyte requiring disposal as a hazardous waste, the hexavalent chromium concentrations in the catholyte, and the labor required for manually pumping out, storing, and disposing of spent catholyte solutions. As a result of the membrane leakage, the vendor has indicated an improvement in the quality control of their membrane and tube formations. No membrane can be totally guaranteed against leakage, however, and the sulfate catholyte as currently formulated should not be used on an in-line chromic acid stripping solution at high temperatures. The system can be used on an in-line solution that is not sensitive to sulfate contamination (i.e., the hard-chromium-plating tank). Alternatively, the system could be operated in a batch mode and the solution could be treated with barium carbonate



TABLE 7. CONCENTRATIONS OF CONTAMINANT METALS
IN CATHOLYTE FROM CHROMIUM PLATING
(mg/L)

Contaminant	Liquid	Sludge
Primary		
Hexavalent chromium	35 ^a	270 ^b
Total chromium	53.4	158,000
Copper	<0.006 ^c	14,500
Iron	0.02	11,800
Nickel	<0.02	2,050
Noncritical		
Aluminum	23.2	<6
Barium	<0.001	80.9
Cadmium	<0.002	611
Calcium	0.463	5,740
Magnesium	<0.002	962
Manganese	<0.002	373
Silicon	<0.04	497
Sodium	25,300	48,900
Zinc	<0.008	1,640

^a Before treatment with sodium metabisulfite. One sample measured 810 mg/L hexavalent chromium.

^b After treatment with sodium metabisulfite for hexavalent chromium reduction.

^c Not detected. The concentration shown is the detection limit for the analyte.

^d Other metals analyzed for but not detected were antimony, beryllium, cobalt, potassium, silver, thallium, and vanadium.



if sulfate contamination is discovered. Finally, the vendor has indicated the development of a catholyte that does not contain sulfate and could therefore be used in-line on the high-temperature chromic acid stripping solution. The vendor has also indicated that a system has been developed whereby any leakage would be from the process solution into the catholyte rather than vice versa.

The volume of catholyte that must be disposed of as a hazardous waste could be addressed by using a filtration system to minimize the sludge volume. This filtration could occur either at the filter press of the wastewater pretreatment plant, or a filter could be installed on the catholyte drum itself. With the installation of a filter on the catholyte drum, the solution could be filtered, chemically adjusted, and reused.

Finally, the hexavalent chromium concentration in the catholyte needs to be addressed; otherwise, the entire catholyte must be disposed of as a hazardous waste. The catholyte could be treated in the catholyte drum by adding sodium metabisulfite or the proprietary alkaline reducing agent. The catholyte could also be treated in the wastewater pretreatment plant, but this would involve acidifying the alkaline catholyte and dissolving the hydroxide sludge if the sludge were not removed by filtration prior to the treatment.

Figure 6 presents a schematic diagram showing a summary of options for tank selection, operational modes (batch versus continuous), and catholyte recycling/treatment.

Conclusions and Recommendations

IT recommends the following for ongoing and future implementation:

- 1) Monitor the plating bath and electrodialysis system on a long-term basis to determine the magnitude of reported problems and to verify that the benefits expected from reducing metal contamination are achieved.
- 2) Retest the electrodialysis equipment on the high-temperature chromic acid stripping solution with the new sulfate-free catholyte formulation. This solution offers the greatest potential for direct waste reduction, and the materials of construction of the electrodialysis system were designed for the high temperature.
- 3) Install a pump and small filter press on the catholyte drum to minimize the sludge requiring disposal; recycle the catholyte by adjusting the pH and chemicals when the sludge is removed.



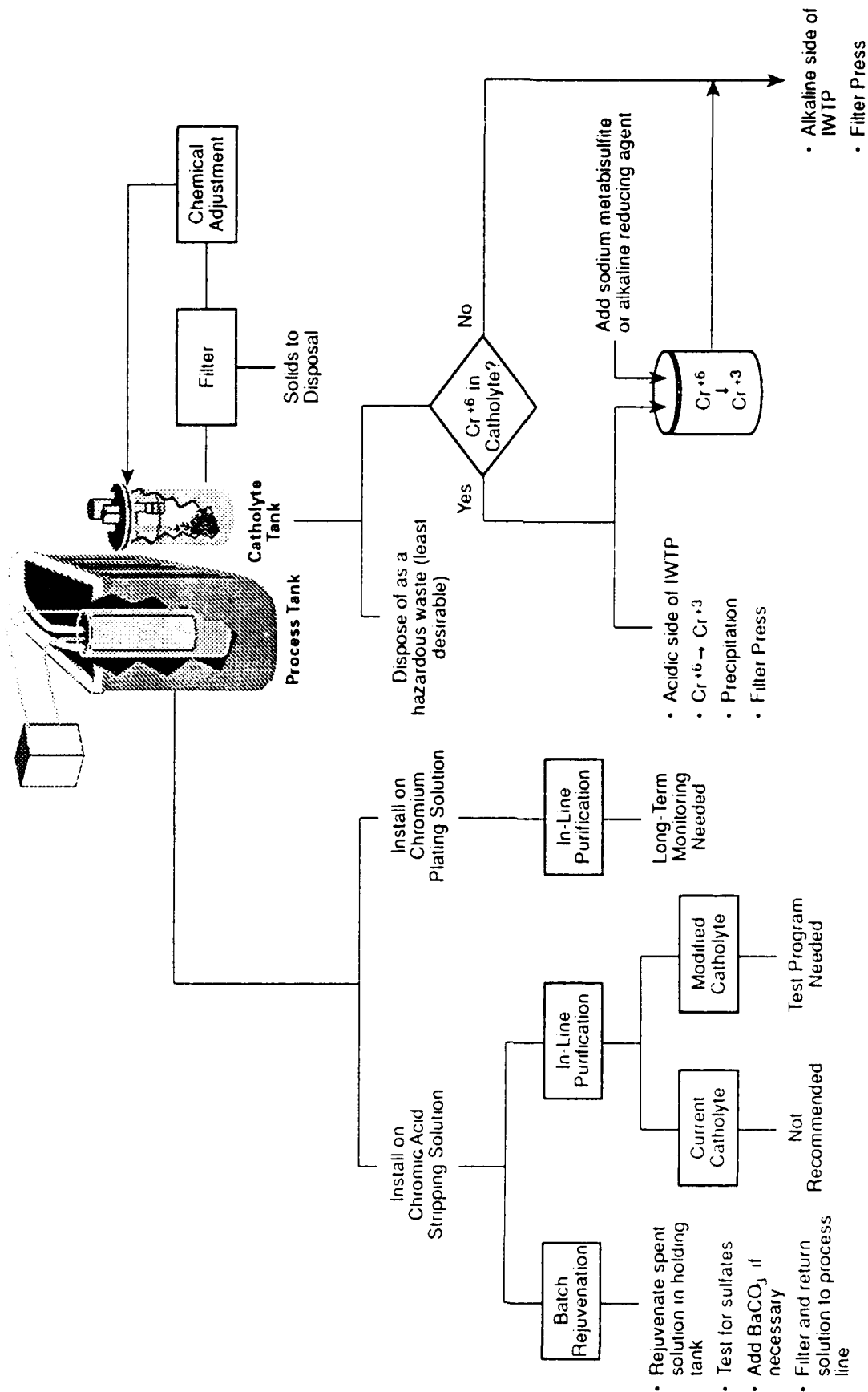


Figure 6. Options for tank selection, operational mode, and catholyte recycle/treatment.

- 4) Work with the vendor to eliminate the hexavalent chromium concentration and to pump any spent catholyte through the alkaline side of the pretreatment plant. Otherwise, pump the catholyte through the chromium reduction side after filtration to remove the hydroxide sludges.
- 5) Test the electrodialysis process on a chromate conversion coating tank, which would require a three-compartment (rather than a two-compartment) cell and closer pH control.
- 6) Test a closed-loop system in which chromium would be removed from the rinse water by ion exchange. Electrodialysis cells would be placed in the process solution to maintain bath quality and would also be used to recover the ion-exchange regenerant solutions.

In conclusion, the electrodialysis cell was successful in significantly reducing contaminant metal concentrations, including trivalent chromium, in chromic acid solutions. For the plating bath, longer-term monitoring will be needed to verify the expected ultimate benefits of increased plating efficiency, increased bath quality, and reduced waste generation. Several concerns arose during the test program. These concerns can be met, however, by selecting the proper tank and mode of operation, testing a new catholyte formulation, or making minor modifications to the existing electrodialysis system to reduce the labor required for operation.

PARTICULATE FILTRATION OF AN ALKALINE PAINT STRIPPER AT LETTERKENNY ARMY DEPOT

The mission of Letterkenny Army Depot (LEAD) in Chambersburg, Pennsylvania, is to overhaul, rebuild, and test wheeled and tracked combat vehicles, missile systems, fire-control systems, and associated secondary items. As part of the refurbishing process of various components and equipment, LEAD uses several chemical stripping operations. Disassembled steel parts coated with metal-based paints containing natural-resin binders are stripped by using a 2,500-gallon alkaline paint stripping solution consisting of sodium hydroxide, sodium gluconate, and various trace compounds. The process tank is 18 ft x 4 ft x 6 ft deep and is operated at 190 to 210°F. Parts may remain in the solution up to 24 hours. Aluminum parts are not stripped in alkaline solutions because these solutions chemically attack such parts.

During the use of a paint stripper, paint is removed and either settles to the bottom as a sludge or remains suspended in the solution. This sludge continues to react with the paint stripper in a saponification reaction, as shown by the following equation:





As this equation indicates, continued contact between the paint sludge and the paint stripper results in consumption of sodium hydroxide, which ultimately reduces the cleaning and stripping capacity of the solution. In addition, buildup of sludge on the bottom of the tank creates operational problems in fitting large parts in the bath that require the entire bath depth. When the required chemical makeup and the operational problems become excessive, the bath is dumped and disposed of as a hazardous waste. At this time, the sludge often must be chipped off the sides and bottom of the tank, which is a labor-intensive process. Each time the tank is emptied (about twice a year), approximately 2,200 gallons of alkaline solution and three 55-gallon drums of sludge are disposed of.

During this USATHAMA-sponsored project, several technologies were considered for removing the particulates in the paint stripper solution with the goal of achieving a longer useful life and a resulting decrease in hazardous waste generation. A pressure filtration system was selected, purchased, and installed by USATHAMA for continuous removal of the paint sludge from the alkaline paint stripping bath. A test plan was then prepared and pursued to determine the effectiveness of particulate removal and the subsequent effect on hazardous waste generation.

Technology Selection

In the initial phase of the project, several technologies were investigated, including bag filtration, centrifugation, gravity belt filtration, vacuum filtration, hydrocyclone, microfiltration, sedimentation, and skimmers. The text that follows presents a summary of these technologies and the rationale for selecting pressure (bag) filtration.

- Pressure (bag) filtration is capable of rapid filtration, which speeds up difficult separations that would otherwise be slow. Other advantages are that the equipment is typically compact and has a relatively low capital cost. Also, the ability to change the bag pore sizes offers flexibility in removing particles of different sizes.
- Centrifuges have higher capital and operating costs than do pressure filters. The higher maintenance costs are due to the high-speed rotating components. Other disadvantages are the low flexibility with rotational speed and liquid throughput, and the fact that the size of particles removed cannot be easily adjusted.



- ° Gravity (hydrostatic) filtration is a simple technology with low capital costs and easy maintenance. Because of the low pressure applied by gravity, this technology is only suitable for easy-to-filter materials. The equipment is typically large and requires a large amount of floor space. Previous testing at LEAD on the alkaline stripper solution showed excessive foaming due to the detergent action of sodium hydroxide and soaps formed in the saponification reaction.
- ° Vacuum filtration provides a higher pressure differential than gravity, and it is good for relatively freely-filtered materials. The capital and operating costs of this technology are high, the operation is complex, and it requires more floor space compared with pressure filtration. Foaming problems similar to those observed with gravity filtration could occur.
- ° Hydrocyclones are useful for separating large, regular-shaped particulates, but their success has been limited for separating finer, irregular-shaped particles such as those that may be generated in the alkaline paint stripper bath. Effluent solids would still contain large amounts of useful stripping solution, and additional equipment would be required for further separation.
- ° Microfiltration would require an additional device to effect the final separation of the concentrated solids stream. The technology contains numerous components and requires a lot of space. The durability of the membrane element is variable, and frequent element replacement could be required. The large amounts of sludge in the alkaline stripping solution could result in frequent plugging of the membranes. Because of the high pH of the alkaline solution, identifying a suitable membrane material would be difficult.
- ° Sedimentation is a slow process, and it cannot be used to separate fine particles from solution. The settled material still must be separated from the rest of the settling chamber. In essence, the alkaline paint stripper tank now used is a settling chamber.
- ° Skimmers are useful for removing solids on the tops of solutions. Although the alkaline paint stripper does have some solids material floating on the surface, this material does not present as big of a problem with solution depletion as does the suspended and settled sludge.

Based on the selection rationale, pressure filtration was chosen for the removal of paint particulates from the alkaline paint stripper bath. The following is a brief review of applicable pump technologies:

- Centrifugal pumps contain a high sheer, which could break down the paint particulates. These pumps are not suitable for alkaline solutions with a high solids content or large pieces of metal (such as bolts).
- Diaphragm pumps, with their slow speed and large valves, can transfer delicate materials when the degradation of the solids is not desirable; however, these pumps tend to be inefficient and noisy. Also, they were determined to be inappropriate for the pressure and flow rates required for this application.
- Progressing cavity pumps are well suited for pumping liquids with high solids content or high viscosities, and they can pass solids and large pieces. The low speed and low sheer of these pumps will not cause degradation of the paint pieces into smaller sizes.

Based on the characteristics of the three types of pumps, a progressing cavity pump was chosen to be used with the pressure filtration system for this project.

Figure 7 is a schematic of the system selected, designed, and installed for this project, and Figure 8 is a picture of the equipment. The system was assembled on a skid and placed near the alkaline paint stripper tank. The alkaline paint stripper solution is pumped from one end of the tank, through the filtration system, and returned to the opposite end of the tank. The system consists of a progressing cavity pump capable of transporting 50 gallons per minute at a maximum total system pressure drop of 125 psi, three filtration units in series fitted with bag filters (available filter sizes = 1 to 400 μm), a mixing eductor on the return line to provide agitation, a control panel, controls to shut down the pump in case of high or low pressure, a high-pressure bypass valve to prevent overpressurization, pressure gauges, sample valves, drain valves, shutoff valves, and a high/low-pressure alarm.

Implementation of the Test Program

This project consisted of essentially three phases: 1) installation and startup, 2) sludge removal, and 3) continuous operation. A test plan was prepared to collect quantitative data on the particulate removal efficiency and ultimate waste reduction achieved by the process. Because of the mechanical problems encountered in the first two phases of the project, quantitative data on the system characteristics were not obtained by the end of the project schedule (April 1991). The following is a brief history of the project, the problems encountered, and the solutions to these problems.



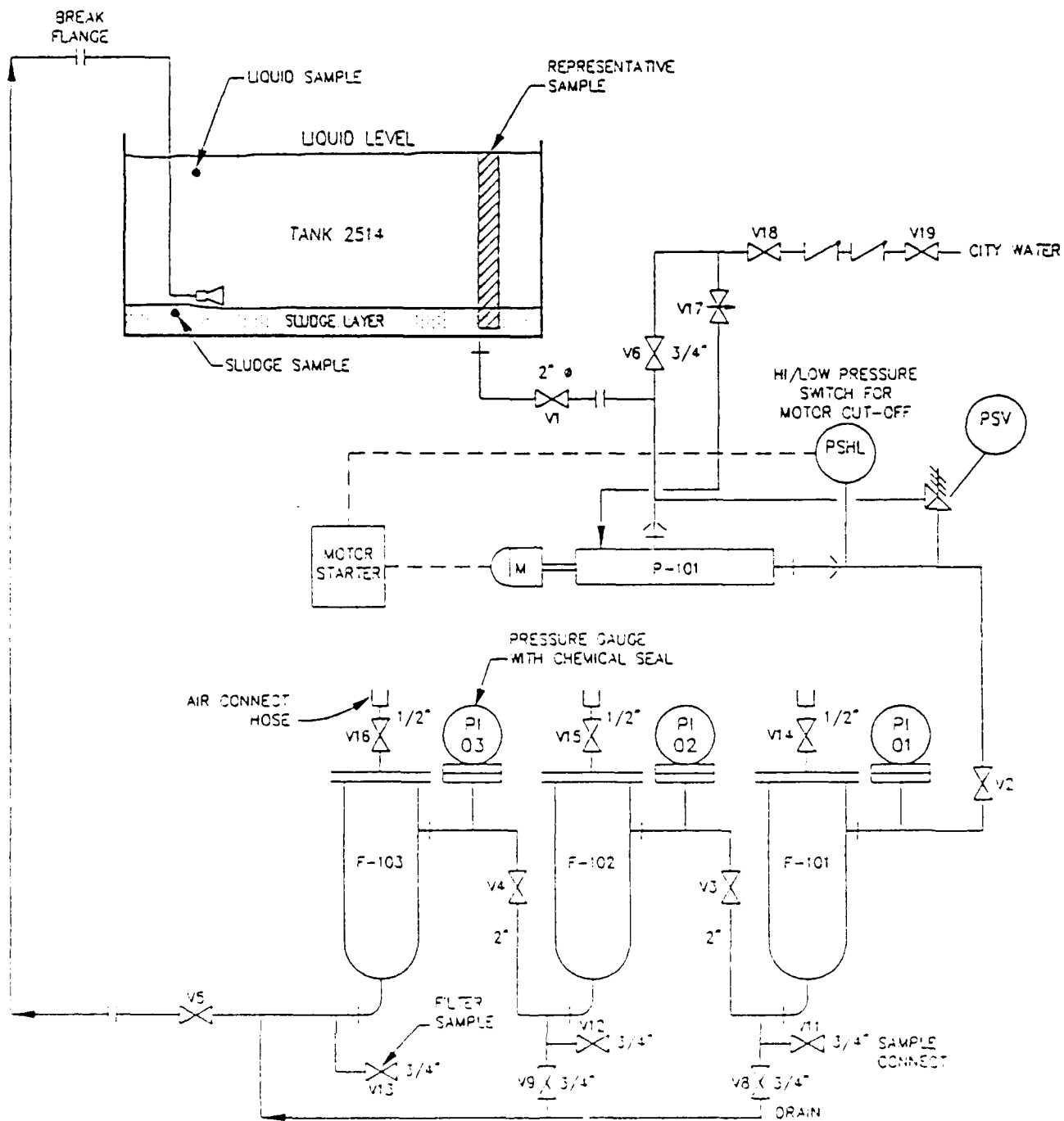


Figure 7. Process sketch for the alkaline paint stripping solution particulate filtration system.

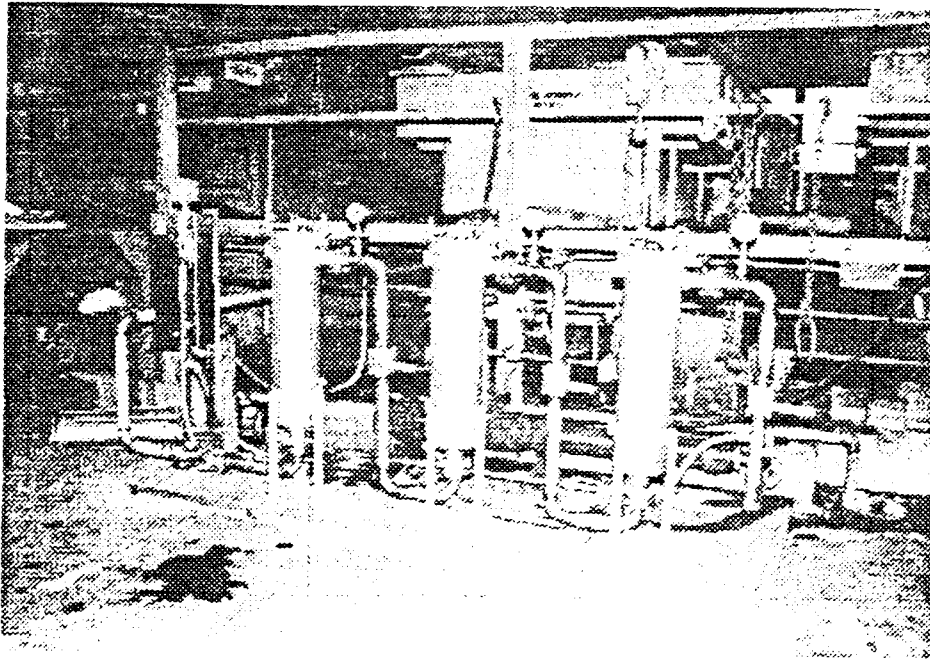


Figure 8. Paint stripper particulate filtration system installed at Letterkenny Army Depot.

Table 8 summarizes (by phase) the mechanical problems encountered and the actions that were taken to rectify these problems. During the installation of the system, a faulty weld on the progressing cavity pump was discovered. The weld was repaired by the manufacturer, and the pump was returned to the site. The filtration system was then tested for leaks and operated to filter the alkaline paint stripper bath with a combination of 50 , 5-, and 1- μm bags. The 5- μm bag blinded within 5 minutes. The bag sizes were increased to 200, 100, and 50 μm . After 20 minutes, the polyester bag material disintegrated. The manufacturer's literature used in the selection of this material was found to be inaccurate. The nylon bags ordered to replace these bags were found to be sewn together with polyester thread, which also dissolved. Additional problems encountered included failure of the O rings on the filter basket and in the filter housing groove at the welded or glued seam, and the motor and gear reducer couplings on the pump going out of alignment because of either loose pump and drive mounting bolts or improper shimming of the pump. Some of these problems were corrected during this phase of the test plan. The equipment was temporarily shut down to make additional repairs and to order the parts required for continued operation of the system.

The problems encountered and addressed in Phase 1 resulted in additional time being spent at LEAD during Phase 2 to gather data and operating experience on the



**TABLE 8. PROBLEMS ENCOUNTERED DURING IMPLEMENTATION OF TEST PLAN FOR
FILTRATION OF ALKALINE PLANT-STRIPPING SOLUTION**

Phase	Equipment/ system item	Problem encountered	Solution
1	Tank lining	Asbestos used as insulation.	Removed by LEAD personnel before installation.
1	Pump	Faulty weld.	Repaired by manufacturer.
1	Filter bags	Polyester bag material specified by manufacturer's literature disintegrated.	Replaced by nylon filter bags.
1	Filter bags	Replacement nylon bags had been sewn using polyester thread, which disintegrated.	Bags were stapled temporarily, then replaced by nylon bags sewn with nylon thread.
1	O-rings on filter basket	Failed at seam.	Replaced by molded (no seam) o-rings; upgraded to Teflon.
1	Pump	Motor and gear reducer couplings went out of alignment.	Skid was leveled and pump was realigned.
2	Sludge layer	Significant sludge layer had accumulated on the tank bottom after 63 days of use.	Manual raking procedure was developed.
2	Rack on tank bottom	Interfered with raking process.	Removed temporarily.
2	Filter housing bolt	Corrosion occurred because bolt was cadmium-plated carbon steel rather than the specified stainless steel.	Replaced by LEAD.
2	Flange gasket	Leak from chemical attack although neoprene material was specified by manufacturer.	Upgraded to Teflon and replaced.
2	Pressure gauges	Failure due to overpressurization.	Replaced; high-pressure relief valve installed.
2	Valves	Failure of two valve seals due to overpressurization.	Valve seals were replaced; high-pressure relief valve was installed.

(continued)

TABLE 8 (continued)

Phase	Equipment/ system item	Problem encountered	Solution
2	Filter basket	Failed at seam because of overpressurization.	Replaced; high-pressure relief valve installed.
2	High-pressure cutoff controls	10-second delay allowed sufficient pressure to damage parts.	High-pressure relief valve and backup system installed in Phase 3.
2	Tank agitation	Tank agitation and return velocity of filtered solution were insufficient to transport sludge to suction inlet.	Installed eductor.
3	Solution mixing	During mixing of a new solution, powder dissolved very slowly.	Filtration unit was used to provide additional turbulence.

equipment. The initial test plan specified operating the filtration system on a clean bath before any sludge had accumulated. Because of the startup delays discussed earlier, however, a significant layer of sludge had accumulated on the bottom of the bath (after 63 days of operation of the stripping bath) when Phase 2 was initiated. The agitation of the stripping solution was not sufficient to transport the large volume of heavy sludge along the entire tank bottom to the suction line of the filtration system. Therefore, the solution had to be raked manually toward the filtration suction line. Because of the large amount and size of the accumulated solids, a 400- μ m bag was placed in one filter housing and the other two were left empty. Monofilament bags (as opposed to mesh) were used because the sludge could be removed and the bags reused. Approximately 5 to 15 pounds of sludge was removed each time the bag required emptying. This method permitted the removal of 250 to 300 pounds of sludge from the tank within 12 hours by raking; this is equivalent to half of a 55-gallon drum. For comparison purposes, cleaning the bath after 6 months of operation produces approximately three drums of sludge.

To increase the ease of operation and to minimize waste generation, filter bags should require only infrequent changes and be reusable. During the second project phase, the filter bag collection efficiency was determined. Although monofilament bags are more expensive than mesh bags, this is offset by their ability to collect more sludge per weight of bag material and the fact that they can be reused numerous times. Upon blinding, mesh bags must be disposed of, whereas monofilament bags can be reused. During the removal of suspended solids, mesh filter bags were capable of collecting between 1.0 and 3.6 pounds of solids per pound of bag material ($\text{lb}_s/\text{lb}_{bm}$); monofilament bags were capable of collecting 5.3 $\text{lb}_s/\text{lb}_{bm}$. When filtering



the alkaline sludge layer, monofilament bags were capable of collecting greater than 74 lb_s/lb_{bm}, and the bags were reused more than 20 times without any observable detrimental effects.

Based on the experience gained during this phase of the project, two methods of operating the equipment are recommended: 1) continuous removal of suspended solids to maintain a clean bath and to prevent or minimize the accumulation of sludge on the tank bottom, and 2) periodic removal of settled sludge to prevent buildup to the point where it becomes an operational problem and to prevent reaction with active bath ingredients.

Mechanical problems observed during this phase included corrosion of a filter housing bolt that was not made of the specified material and a leaking flange gasket (Table 8). Several pieces of equipment also failed because of overpressurization of the system, including pressure gauges, valve packing, and a basket seam. The pump controls included a 10-second delay between sensing an overpressure condition and shutting off the pump. Apparently, this delay was sufficient time for equipment damage to occur. The equipment was temporarily shut down to determine if the flange had leaked as a result of mechanical failure (from overpressurization) or chemical attack, and to install a high-pressure relief and emergency backup system.

The third phase of the operation entailed correction of the problems encountered during Phase 2, installation of the high-pressure relief system, installation of an eductor on the return line, and leaving the system on site at LEAD for continuous operation. After the repairs and installation were completed, the equipment began operation on a fresh alkaline solution. During the mixing of this solution, it was discovered that the alkaline stripping powder dissolves very slowly, and the progressing cavity pump was used effectively to circulate the solution through the filtration system (without filter bags) to help mix the powder. The eductor appeared to be successful in increasing the agitation of the solution. The project ended within a week after these repairs were made, and the project schedule did not allow for additional characterization of the bath or monitoring of the desired impact of sludge removal. Since that time, however, LEAD engineers have indicated that the system is operating properly. The ultimate effect of the filtration system on waste reduction can only be determined by long-term (> 1 year) monitoring of the alkaline solution and filtration system, including the amount of chemicals added to the bath, the bath depletion rate, and the amount of waste generated.

Conclusions and Recommendations

Although mechanical difficulties that occurred during this project prohibited collection of the quantitative data specified in the test plan, the filtration system appears to be removing sludge from the paint-stripping solution. The following is a list of the expected ultimate benefits of operating the filtration system:



- 1) Increased agitation and circulation will aid dissolution of the chemical powder used to make up the solution.
- 2) Elimination or significant reduction of sludge formation on the bottom of the tank. Reduction of suspended solids.
- 3) Reduction in usage of sodium hydroxide. (Sodium gluconate is thermally unstable and decomposes with time, and previous studies at LEAD show a correlation between sodium gluconate depletion and temperature. Filtration is not likely to have any effect on sodium gluconate usage.)
- 4) Increase in bath life and reduction of liquid alkaline solution that must be disposed of. The ultimate goal is to dispose of six barrels of sludge per year while replenishing only the active ingredients.
- 5) Reduction in manpower required to remove sludge, and elimination or reduction in hazards involved in entering the tank to remove sludge.

Because of the time constraints of this project and the lack of quantitative data obtained, additional effort by LEAD or USATHAMA is needed to verify that the above benefits are achieved. In addition, operational or equipment changes would allow for greater ease and efficiency of operation. The following changes are recommended:

Operating changes:

- 1) Operate the system without filter bags while dissolving the chemical powder to make up a solution.
- 2) Start filtration with a clean bath to eliminate the necessity for the labor-intensive sludge raking process.
- 3) During chemical makeup of the bath, include other additives that are required for the solution to be fully effective.
- 4) Check for sludge buildup on a weekly basis, and perform raking process if needed.
- 5) Implement a regular maintenance program.

Filter bag changes:

- 6) Use monofilament rather than mesh bags to reduce waste volume associated with bag disposal.



- 7) Determine the most effective filter bag combination.
- 8) Determine the most efficient filter bag to collect solids during sludge raking.
- 9) Determine the effective life of the monofilament bags.
- 10) Reduce micrometer rating of bags as larger particles are removed.

System and equipment modifications:

- 11) Elevate grates above the bottom of the tank to increase turbulence.
- 12) Relocate pressure gauges to avoid accidental damage when opening filter housings.
- 13) Install braces on the equipment to reduce system vibration.

EVALUATION OF HIGH-VOLUME, LOW-PRESSURE (HVLP)
PAINT APPLICATION SYSTEMS AT
SACRAMENTO ARMY DEPOT

This project involved testing commercially available low-cost HVLP paint spray equipment with expected high-transfer efficiencies and testing Sacramento Army Depot's (SAAD) present paint spray equipment for comparison purposes. The paints used during the test were two types of chemical-agent-resistant coatings (CARCs) currently used in production at SAAD. The evaluations were conducted in two phases. Phase I (November 1990) included the purchase and testing of three low-cost HVLP systems. Phase II (March 1991) included the testing of turbine HVLP and conventional paint spray systems currently used at SAAD.

This project is important to the depots because using paint spray guns with high transfer efficiencies would decrease the amount of waste generated by painting operations through reduction of the overspray collected in the paint booth particulate filters. It also would decrease volatile organic compound (VOC) emissions by reducing the quantity of paint used. The trend toward legislated transfer-efficiency requirements provides additional motivation for investigating HVLP systems.

SAAD conducted testing between mid-1987 and early 1988 to select the most efficient equipment available for spray paint application. Five types of spray guns were tested: conventional, electrostatic, air-assisted airless, airless, and the turbine HVLP system. Of the spray equipment tested, the turbine HVLP system proved to have the highest overall paint transfer efficiency on the paints used and the parts processed at



SAAD. As a result of these early tests, the turbine HVLP system was approved by Sacramento County Air Quality Management District (SCAQMD) for SAAD to use for meeting legislation requiring a transfer efficiency of 65 percent.

Based on the results of testing conducted by SAAD in 1987 and 1988, SAAD purchased two turbine HVLP systems manufactured by Can-Am Engineered Products Inc. Each system is equipped with four guns, and the cost per system was approximately \$25,000; however, more economical (i.e., less than \$1000 per gun) HVLP systems are available. For this reason and because of its ongoing work in this area, SAAD volunteered to be the host facility for the USATHAMA paint-transfer-efficiency tests.

The objectives during the testing at SAAD were as follows:

- 1) To determine the suitability of low-cost HVLP spray-painting equipment for applying one- and two-component polyurethane coatings to small and medium-sized parts.
- 2) To compare the results obtained by the turbine HVLP system and conventional paint spray systems currently in use by SAAD with those obtained by the low-cost HVLP equipment when the same test plan procedures (with minor exceptions) were used for testing.
- 3) To measure the transfer efficiency of the equipment tested.
- 4) To determine whether heated air would improve transfer efficiency and coating finish when HVLP equipment is used.

The HVLP spray guns used during Phase I were chosen for the following reasons: the guns were able to meet the low cost requirement set by SAAD (<\$1000 per gun without heater), they were readily available on the commercial market, and they were representative of the different types of HVLP guns currently available. All three HVLP paint spray guns tested use plant air. The Binks Mach 1 (Model 97 x 95P) and Graco Help 1000 (Model 110-697) guns use a venturi to convert the plant air pressure (typically 120 psi) to less than 10 psi inside the gun, whereas the DeVilbiss gun (Model JGHV-503) uses a regulator attached to the paint booth wall. An explosion-proof heater was purchased with the DeVilbiss model to investigate using heated air to improve paint transfer efficiency.

The turbine HVLP system is capable of supplying each gun with a stream of low-pressure air (less than 10 psi) at an elevated temperature (up to 260 °F). The SAAD conventional paint spray gun tested during the second phase of testing was manufactured by DeVilbiss (Model MBC-510-30EX). Unlike HVLP paint spray equipment, which operates at a gun outlet pressure of less than 10 psi, the outlet



pressure from this type of spray gun is typically in the 20 to 60 psi range. Paint atomization is accomplished by mixing the paint with high-pressure shop air (typically 120 psi).

All of the guns were tested with the following paints:

- 1) One-component chemical-agent-resistant coating (CARC) - Hentzen moisture cure polyurethane paint (CARC MIL-C-53039A), 3.5 lb VOC per gal.
- 2) Two-component enamel replacement- Cardinal Company polyurethane paint (alternate to TTE-527, TTE-529, and TTE-489), 2.8 lb VOCs per gal.

The Hentzen CARC paint is a very gritty paint (contains silicon sand), whereas the Cardinal paint is quite viscous. These "worst case" paints were chosen by SAAD to present a unique challenge to the spray guns used during the transfer efficiency tests.

Both small and medium-sized parts were used for the transfer efficiency tests at SAAD. Previous testing conducted at SAAD on large parts indicated that high transfer efficiencies were achievable regardless of the type of spray paint equipment. As a means of assuring equal testing between guns during each demonstration, identical parts (i.e., type, size, and number) were used for each gun. Although identical parts were not available for the second phase of testing, parts were selected that were very similar in shape and size to those used during the first phase of testing.

A digital scale was used to weigh test parts. This scale was capable of weighing parts up to 70 lb to the nearest 0.5 g and was accurate within ± 0.25 g.

As shown in Table 9, 45 separate trials were conducted during the first phase of testing and 24 were conducted during the second phase. Results of the paint transfer efficiency test during the trials for both demonstrations are summarized in Table 10. Transfer efficiencies were calculated as follows:

$$\% \text{ transfer efficiency} = \frac{(\text{weight of solids applied to parts, g})}{(\text{weight of coating applied g}) \times (\% \text{ solids in coating})} \times 100$$



TABLE 9. MATRIX OF TRIALS FOR TESTING AT SAAD

Part size	Phase 1				Phase 2	
	Binks Mach 1	Graco Help 1000	DeVilbiss System 89 (nonheated)	DeVilbiss System 89 (heated)	Can-Am	Conven- tional DeVilbiss
CARC (Hentzen)						
Small	3	3	3	3	3	3
Medium	3	3	3	3	3	3
PUP (Cardinal)						
Small	3	3	3	0	3	3
Medium	3	3	3	3	3	3

Test Results

Table 10 presents the results of the test program. The Phase I test results for the low-cost HVLP paint spray equipment ranged from a low of 11.2 percent to a high of 64.6 percent. The mean paint transfer efficiencies for small parts ranged from 16.1 to 27.6 percent. Mean paint transfer efficiencies for medium-sized parts ranged from 49.4 to 58.2 percent. The Phase II test results with the Can-Am turbine HVLP paint spray equipment ranged from a low of 28.6 percent to a high of 67.6 percent. The Can-Am mean paint transfer efficiencies for small parts ranged from 30.1 to 36.7 percent. Mean Can-Am paint transfer efficiencies for medium-sized parts ranged from 60.7 to 64.3 percent. The Phase II test results of the DeVilbiss conventional paint spray equipment ranged from a low of 26.7 to a high of 63.9 percent. Average DeVilbiss conventional equipment paint transfer efficiencies for small parts ranged from 28.3 to 30.5 percent. Average DeVilbiss conventional equipment paint transfer efficiencies for medium-sized parts ranged from 61.7 to 63.3 percent.

The test data collected during the test and presented in the test report include such information as part size, type of equipment tested, manufacturer and model number of the paint spray equipment, operating conditions (i.e., air and fluid pressures, orifice and needle settings, outlet gun pressures, spray booth exhaust velocity, spray booth dimensions, relative humidity, air temperature, and time of day), details on the paint coating (i.e., sample number, manufacturer, type of coating, MIL spec. number, trade name, batch number, and shelf life), VOC and percent solids contents of the applied coating (i.e., per Material Safety Data Sheet and calculations based on laboratory results of paint samples collected), quality assurance inspection results, and the measured paint transfer efficiency results from Phase I testing.



TABLE 10. RESULTS OF SAAD PAINT TRANSFER EFFICIENCY TESTS

Trials	Transfer efficiencies, %									
	Phase 1					Phase 2				
	Binks	Avg.	DeVilbiss	Avg.	Graco	Avg.	Can-Am	Avg.	Conventional	Avg.
CARC (Hentzen)										
63.60% solids (all trials)										
Small Trial 1	19.8	27.6	24.1	25.1	23.1	25.8	30.0	36.7	30.4	30.5
Small Trial 2	30.9		25.7		19.1		36.4		31.3	
Small Trial 3	32.2		25.6		35.3		43.6		29.8	
Medium Trial 1	62.2	58.2	59.1	52.7	64.6	54.7	67.6	64.3	61.8	61.7
Medium Trial 2	62.4		55.9		56.6		64.4		62.2	
Medium Trial 3	50.1		43.2		42.8		61.0		61.2	
Medium heated Trial 1			54.9	50.5						
Medium heated Trial 2			53.2							
Medium heated Trial 3			43.3							
PUP (Cardinal)										
75.21% solids (Binks & DeVilbiss trials)										
75.12% solids (Graco trials)										
Small Trial 1	11.2	16.1	20.8	18.7	16.4	17.3	32.3	30.1	27.4	28.3
Small Trial 2	18.9		20.1		16.7		28.6		26.7	
Small Trial 3	18.1		15.1		18.9		29.4		30.8	
Medium Trial 1	58.8	56.0	56.6	55.8	49.4	49.4	63.2	60.7	63.8	63.3
Medium Trial 2	56.9		60.1		52.1		59.2		62.3	
Medium Trial 3	52.3		50.7		46.6		59.6		63.9	
Medium heated Trial 1			55.5	56.2						
Medium heated Trial 2			60.3							
Medium heated Trial 3			52.8							

Conclusions and Recommendations

Based on the results obtained from the paint transfer efficiency demonstrations conducted at SAAD, the following conclusions have been drawn:

- 1) None of the three low-cost HVLP paint spray guns clearly outperformed the other with respect to transfer efficiency or coating finish. Small variations in measured transfer efficiencies were probably due to the paint operator rather than the paint spray equipment.
- 2) With the particular model tested, the use of heated air had no major effect on improving the transfer efficiency or the coating finish.
- 3) None of the HVLP equipment tested at SAAD on small parts with either of the coatings achieved a measured transfer efficiency ≥ 65 percent. The transfer efficiency averages ranged from 16.1 to 36.6 percent.
- 4) With the exception of the Can-Am turbine system in one test run, none of the HVLP equipment tested at SAAD on medium-sized parts with either of the 2 coatings achieved a measured transfer efficiency ≥ 65 percent. The transfer efficiency averages for the low-cost HVLP equipment ranged from 49.4 to 58.2 percent. The average transfer efficiencies for the turbine HVLP equipment ranged from 60.6 to 64.4 percent. It should be noted, however, that different parts and a different paint spray booth were used in the testing of the low-cost HVLP guns.
- 5) The conventional paint spray gun tested at SAAD achieved paint transfer efficiencies approaching those of the HVLP types on both small and medium-sized parts when operated at low outlet air pressures (i.e., approximately 20 psi).
- 6) The conventional paint spray gun tested at SAAD achieved proper paint atomization (i.e., proper coating lay) for both coatings while operating at low outlet air pressures (approximately 20 psi).

Based on the experience and data obtained during this project, the following recommendations are made:

- 1) New variations of HVLP paint spray guns are now available on the market. These "next generation" models should be investigated.
- 2) Improving paint transfer efficiency and coating finish by heating the paint fluid should be investigated. Unlike heating the atomization air, there is less potential for heat loss due to heat transfer or venturi effects.



REFERENCES

Final reports will be available soon for all the projects discussed in this paper. These reports can be obtained from USATHAMA or IT. The references are provided below:

- 1) Evaluation of Electrodialysis for Chromic Acid Purification/Recovery at Corpus Christi Army Depot, USATHAMA Report No. CETHA-TS-CR-91032.
- 2) Particulate Filtration of an Alkaline Paint Stripping Solution at Letterkenny Army Depot, USATHAMA Report No. CETHA-TS-CR-91033.
- 3) Evaluation of Transfer Efficiencies of High-Volume Low-Pressure Paint Application Systems at Sacramento Army Depot, USATHAMA Report No. CETHA-TS-D-12345.

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Degreasing System Pollution Prevention Modification Vs.
Industrial Hygiene Concerns

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INTRODUCTION

The U.S. Environmental Protection Agency's Air and Energy Engineering Research Laboratory (EPA/AEERL) and the U.S. Air Force's Engineering and Services Center have been conducting joint environmental research and applied engineering studies since 1986. These studies are aimed at developing cost effective technologies for control of volatile organic compound (VOC) and toxic compound emissions from Air Force facilities. However, the ultimate value of this joint effort is the development of options for use by the entire industrial community.

This study evaluates the impact of various degreaser modifications, applied to a vapor degreaser to control the emissions of toxic and volatile solvents, upon their concentration in the work environment. It addresses a problem faced by both military depot and commercial degreaser installations: accumulation of potentially toxic concentrations of degreasing solvent vapors in the work areas and the emissions of these solvents to the atmosphere. Although it is possible to control atmospheric emissions with conventional control technologies, the resulting cost may be prohibitive for some operations. Engineering to provide a safe work environment typically employs large volumes of dilution air, a practice that can greatly amplify the cost of emission control.

The study was based on research conducted by the EPA in early 1980 and relies heavily upon the experience gained during that study.

TEST PROGRAM OBJECTIVES

The study was conducted at Wright-Patterson AFB, OH. Its purposes were to qualitatively define the reduction in emissions afforded by each modification, to measure the concurrent workplace exposure, and to identify which of the modifications support safe conditions in the workplace. The study evaluates relatively simple degreaser modifications designed for operation with or installed on existing degreasers.

Several years before the evaluation was conducted, a lip vent had been installed on the degreaser to decrease methyl chloroform (1,1,1-trichloroethane or TCA) levels in the workplace. This study was designed to show that a safe workplace concentration can be maintained without the lip vent, which was suspected to be the cause of excessive emissions to the atmosphere from the degreaser.

TEST CRITERIA

The criteria used to define the ability of each control option to maintain a safe working environment while reducing pollutant discharges are based on established Occupational Safety and Health Administration (OSHA) and U.S. Air Force (USAF) exposure limits.



The OSHA 8 hour personal exposure limit (PEL)¹ of 350 ppm and the USAF exposure limit of 43 ppm (12.5% of the PEL) defined criteria for success of the project. Table I lists the OSHA and USAF concentration limits for the project.

Table I Concentration Limit Criteria for TCA

<u>OSHA</u>	<u>OSHA Action Limit, ppm</u>	<u>Study Target Limit, ppm^c</u>
350 ppm 8-hour TWA ^a	175	43
450 ppm STEL ^b	255	56

^a 8-hour time weighted average (TWA).
^b 15 minute short term exposure limit (STEL).
^c USAF engineering control limit.

TEST SITE EVALUATIONS

The evaluation site for this study is a metal fabrication shop located at Wright-Patterson AFB, OH, which uses a Phillips T156S degreaser installed in 1979. The degreasing solvent presently used in the system is TCA. The degreaser is located in an alcove in the metal plating section of the shop. Figure I is a schematic of the plating shop showing the location of the degreaser. Due to the confined and isolated location of the degreaser in the shop, a lip vent was installed to prevent the buildup of potentially harmful levels of degreasing solvent. The lip vent exhausts at a rate of 2500 SCFM (70.75 m³ per minute). It maintains an average breathing zone concentration of 10 ppm. Degreaser system specifications are presented in Table II.

Since the degreaser lip vent has been in operation, the degreaser has consumed approximately 56,000 lb (25,400 kg) of TCA annually. All the solvent loss is presumed to have been emitted to the atmosphere. Preliminary investigations suggested that suction from the lip vent induced the discharge to the atmosphere of a significant portion of the solvent loss from the degreaser.



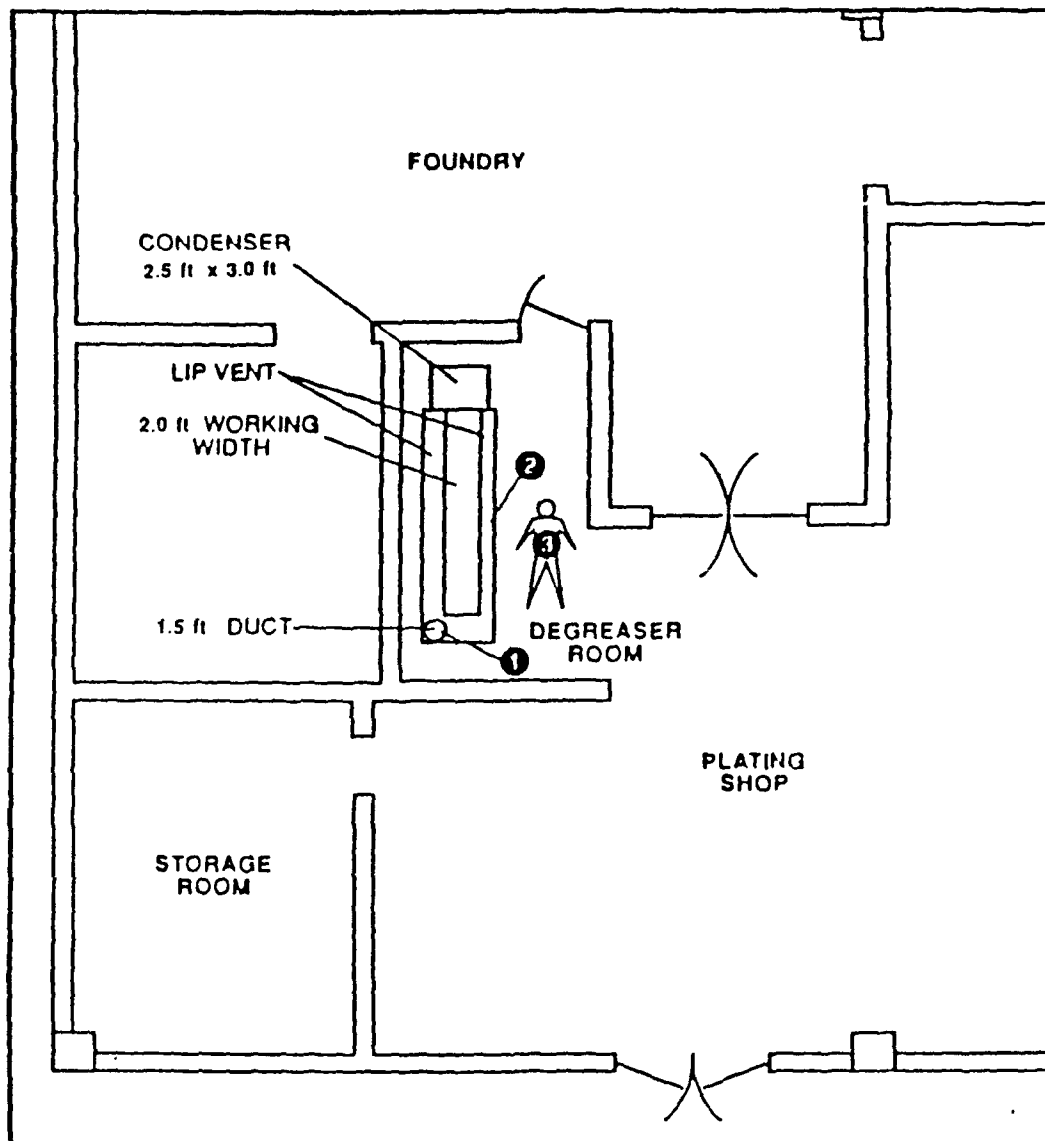


FIGURE 1 Degreaser and sampling locations in the plating shop.

TABLE II Degreaser Specifications

. Model:	Phillips T156S
. Solvent:	1.1.1-Trichloroethane (TCA)
. Working Dimensions:	Length = 15 ft (4.6 m)
	Height = 8.0 ft (2.4 m)
	Width = 2.0 ft (0.61 m)
. Freeboard Ratio:	75% (Before modification)

TEST PROGRAM

The test program was designed to address two main objectives. First, it was designed to quantify the decrease in solvent loss to the atmosphere achieved by the use of selected equipment modifications. A decrease in solvent consumption monitored over a period of time correlates with a decrease in solvent emissions. This value can be compared to the premodification concentration level. Second and equally important the project also quantifies the workplace solvent concentrations that each option allows at three defined locations. These concentration data were used to identify the modification that maintains the workplace concentration within the criteria defined in Table I.

The testing and analytical procedures used for the evaluations include OSHA methods to characterize work area concentrations and both continuous and Tedlar[®] bag sampling methods to characterize duct emissions and ambient concentrations. Three sampling locations were used to ensure compliance with work area safety requirements and to quantify pollutant emission rates. The first, located in the exhaust duct of the lip vent, measured atmospheric emissions. The second, located at the degreaser midpoint, measured work area concentrations at a typical operator's breathing height. The third was located on the operator at his breathing zone.

The stationary midpoint concentration measurement is not a standard OSHA determination. However, it provides a realistic estimate of the relative mean concentration in the degreaser area. It is not indicative of the operator's real exposure. The midpoint reading gives a more conservative estimate of exposure concentration for industrial hygiene evaluations and thus will typically be higher than test results measured at the operator.

Real time measurements were taken using a Miran 1A[™] gas analyzer with continuous digital and strip chart data recording. These measurements were taken in the exhaust duct. Charcoal tube samples were taken in the exhaust duct, at the degreaser midpoint, and on the operator. The Tedlar[®] bag samples were taken for short

term exposure levels at the degreaser midpoint and at the operator's breathing zone.

TESTING SEQUENCE

As noted above, the lip vent was installed to limit concentrations of solvent vapors in the work area. When the lip vent was in operation, the measured work area toxic vapor concentration remained well below the 43 ppm STEL. However, the lip vent was also believed to accelerate the discharge of solvent from the degreaser. A more satisfactory alternative method of control would be one that could both lower exhaust emissions and maintain concentration levels below the industrial hygiene criteria level.

- Three modifications were examined, alone and in combination:
- . Staged decreased lip vent suction: (70 to 0 m³/min)
 - . Freeboard extension: (75 to 100%)
 - . Freeboard chiller: (-29°C)

These options were identified from previous EPA research and do not represent new control concepts.² However their ability to maintain industrial hygiene levels at the levels defined in Table I was only implied in the earlier studies.

The first series of tests evaluated the effect of decreasing and substantially arresting circulation through the lip vent. The vent suction was reduced first to 50% of original flow and then to 0% of original flow. Both emissions rates and work area concentrations were measured. The reduction of flow experimentally demonstrated the environmental cost to employ the lip vent at the top of the degreaser to lower workplace concentrations. At zero flow, it also eliminated the lip vent as a source of emissions.

The second series of tests evaluated the freeboard extension with and without the exhaust lip vent. The freeboard extension was a custom made metal extension to increase the freeboard by 9 in. (0.23 m). The objective of the extension was to create additional containment height within the confines of the degreaser to isolate potential solvent vapors from the environment.

The third series of tests involved the use and evaluation of a custom made freeboard chiller. This option creates a cold air blanket over the solvent layer, causing condensation of solvent back into the solvent bath. The chiller was evaluated alone and in combination with the freeboard extension.

ATMOSPHERIC EMISSIONS AND INDUSTRIAL HYGIENE RESULTS

The uniqueness of this installation was due in part to the location of the degreaser, a recessed area of the shop. This area does not benefit from the natural drafts in the facility due to its recessed location. Based on the operating history of the degreaser, it was determined that the emissions rate was different between summer and winter. This was apparently due to the relative

difference in ambient temperatures between the two seasons. Thus, tests were conducted during both seasons. Tables III and IV present the results of the summer and winter testing series.

The baseline exhaust concentration results taken with the lip vent operating revealed that the major portion of the emissions were discharged via the lip vent duct. Based on the average lip vent exhaust of 2500 SCFM (70 m³/min) and a measured average concentration of 264.4 ppm during winter days and 279.1 during summer days and 37.5 ppm overnight, the estimated emissions values for a working year total 40,000 lb/yr (18,181 kg/yr). This is approximately 70% of the 56,000 lb/yr (25,454 kg/yr).

The baseline operator breathing zone and midpoint concentration were 1.5 and 15.1 ppm, respectively, for the winter months. Similar summer month concentrations were 0.4 and 21.3 ppm, respectively. The operator concentration is relatively low when compared to the midpoint concentration, presumably because the operator moved into and out of the primary degreasing area during monitoring, which is a normal activity of the operator. This would result in a reduced average concentration reading for the operator measurements.

The first option investigated was the reduction of the lip vent flow in stages, half speed 1250 SCFM (35 m³/min), and in the off condition zero flow. These measurements indicate no discernible emissions other than those fugitive emissions measured around the degreaser. The fugitive emissions defined by the breathing zone and midpoint readings recorded a level 550% over the baseline level to 86.4 ppm. Thus it must be concluded that the lip vent does reduce the industrial hygiene concentration to below the criteria level established for the project.

The second option, increasing the freeboard height, was installed and operated without the lip vent. The results indicate that the work area criteria can generally be achieved simply by using the 100% freeboard. However, a limited number of STEL degreaser midpoint readings exceeded the action level, including 85.5 and 71.5 ppm for summer and winter readings, respectively. It is interesting to note that none of the operator readings with this option exceeded the action level criteria. However, because the midpoint excursions indicate a potential to exceed the action level, this option was considered not to achieve the criteria.

The third option utilized a custom made freeboard chiller with and without the freeboard extension. The modification was tested only during the summer, which was considered the most severe test period. The maximum steady state readings were 43.5 (without extension) and 29.2 ppm (with extension).

CONCLUSIONS

The results clearly indicate that the industrial hygiene exposure level can be maintained for an existing degreaser installation. This can be done with a relatively inexpensive



TABLE III Results from Summer Test Series

SAMPLE TYPE/location	Average Concentration (ppm) of 1,1,1-TCA with Control Option				
	Baseline	Reduce lip vent suction	Freeboard extension	Chiller w/o extension	Chiller w/ extension
CHARCOAL TUBE SAMPLES					
Lip Vent Exhaust Duct	347.4	350.0	NS ^a (fan off)	NS (fan off)	NS (fan off)
Degreaser Midpoint	21.3	44.5	39.7	NA ^b	32.0
Operator	0.4	0.8	3.3	NA	4.0
MIRAN 1A/REAL-TIME DATA					
Lip Vent Exhaust Duct - day shift	279.1	312.2	NS	NS	NS
- overnight	NS	47.1	NS	NS	NS
Degreaser Midpoint - day shift	NS	NS	43.0	45.6	29.2
- overnight	NS	NS	NS	25.7	NS
TEDLAR BAG SAMPLES					
Full Shift - Degreaser	15.7	36.0	38.8	41.2	27.2
STEL Average - Degreaser	14.8	30.8	64.3	43.4	23.9
- Operator	1.3	6.1	7.4	5.7	5.8
STEL #1 - Degreaser	13.1	30.9	60.1	43.2	28.6
- Operator	1.7	7.9	5.5	4.4	9.9
STEL #2 - Degreaser	15.6	30.7	85.5	43.5	21.8
- Operator	1.4	4.3	10.6	6.9	5.5
STEL #3 - Degreaser	14.2	NS	47.2	NS	21.3
- Operator	1.2	NS	6.1	NS	1.9
STEL #4 - Degreaser	16.1	NS	NS	NS	NS
- Operator	1.0	NS	NS	NS	NS

^aNot sampled.^bNot analyzed.

TABLE IV Results from Winter Test Series

SAMPLE TYPE/location	Average Concentration (ppm) of 1,1,1-TCA with Control Option			
	Baseline	Reduced lip vent suction	Fan off	Freshboard extension
<u>CHARCOAL TUBE SAMPLES</u>				
Lip Vent Exhaust Duct	391.1	329.5	NS ^a (fan off)	NS (fan off)
Degreaser Midpoint Operator	15.1 1.5	11.4 1.4	86.4 12.1	28.1 4.8
<u>MIRAN JA/REAL-TIME DATA</u>				
Lip Vent Exhaust Duct - day shift	264.4	242.4	NS	NS
- overnight	37.5	39.4	NS	NS
Degreaser Midpoint - day shift	NS	NS	42.2	13.5
- overnight	NS	NS	13.2	11.7
<u>TEDLAR BAG SAMPLES</u>				
Full Shift - Degreaser midpoint	NS	9.2	48.9	45.5
STEL Average - Degreaser midpoint - Operator	17.1 5.2	8.5 <1.0	33.5 46.4	43.2 27.7
STEL #1 - Degreaser - Operator	15.7 5.7	5.0 <1.0	10.0 40.0	71.5 41.2
STEL #2 - Degreaser - Operator	21.0 3.7	17.5 <1.0	9.1 18.9	31.9 17.2
STEL #3 - Degreaser - Operator	14.5 6.3	4.5 <1.0	69.6 61.7	26.2 24.8
STEL #4 - Degreaser - Operator	NS NS	7.0 1.6	45.2 65.1	NS NS

^aNot sampled.

environmentally friendly modification when compared to add-on end-of-pipe systems and without ventilation with massive volumes of dilution air. The freeboard extension can maintain acceptable exposure levels within the OSHA criteria level. However, the more stringent occupational safety standards applied at the military facility may require the use of more active control. The freeboard chiller both with and without the extension satisfied all emission and Air Force industrial hygiene criteria.

REFERENCES

1. U.S. Department of Labor: Air Contaminants-Permissible Exposure Limits, Title 29 Code of Federal Regulations Part 1910.1000: (OSHA 3112). 1989.
2. Gerstle, R.W., V.S. Katari, and E.S. Schindler. Evaluation of Solvent Loss From Vapor Degreaser Systems. EPA-600/2-81-042 (NTIS PB81-176398), March 1981.

EVALUATION OF ALTERNATIVE CHEMICAL PAINT STRIPPERS TO REDUCE TTO DISCHARGE AND MINIMIZE HAZARDOUS WASTE¹

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INTRODUCTION

Background

In 1984 the U. S. Environmental Protection Agency (U.S. EPA) placed a limit of 2.13 mg/l on the allowable concentration of Total Toxic Organics (TTO) which can be discharged from metal finishing operations. Some of the metal finishing operations find it difficult to comply with this regulation when using the popular cold chemical paint strippers. These strippers contain methylene chloride. Besides contributing to TTO, methylene chloride is a suspected carcinogen and is affected by restrictions on emissions of air toxics under amendments to the Clean Air Act. Many of the strippers are also classified as hazardous wastes after use. Disposal of the paint stripper wastes will become more difficult and costly as many of these wastes are banned from land disposal under the U.S. EPA schedule.

Objective

The objective of this study is to identify paint strippers which are operationally effective and environmentally acceptable replacements for methylene-chloride-based paint removers. The goal is to alleviate TTO compliance problems and to minimize environmental and health risks and disposal liabilities.

Approach

To test operational success, alternative stripper formulations were first evaluated in the laboratory. Materials meeting the criteria established for success in the laboratory were tested on a pilot scale. The environmental, health, and safety aspects of the selected strippers were also evaluated to ensure that the candidates are acceptable replacements. The final step in this process is a full-scale field test.

¹ This research was supported by the U.S. Army Toxic and Hazardous Materials Agency (P147.01.16 Evaluation of Alternatives to Toxic Organic Paint Strippers).

EVALUATION CRITERIA FOR AN ACCEPTABLE PAINT STRIPPER

Criteria for a successful paint stripper were developed in collaboration with Sacramento Army Depot (SAAD). The following criteria were selected: (1) acceptable stripping speed (SAAD upper limit of 2 hours), (2) effective for a broad spectrum of coatings, (3) not rapidly evaporated or depleted and easily replenished when it does become depleted, (4) No TTO contributing chemicals, (5) environmentally acceptable, (6) safe to use, (7) relatively easy to dispose, (8) commercially available, (9) easy to procure.

In addition, more specific criteria for environmental, health, and safety evaluation of an alternate paint stripper were selected in cooperation with SAAD. These criteria included factors relating to toxicity (acute and chronic, human and environmental), environmental fate, safety (corrosivity, reactivity, and ignitability), and regulatory restrictions (1).

SELECTION OF COATINGS AND STRIPPERS FOR TESTING

Using knowledge of coatings chemistry, coatings for stripper testing were selected based on common occurrence in the military inventory and, in some cases, because they represented the hard-to-strip end of the spectrum. Generically, the coatings were zinc-chromate alkyd primer with an alkyd topcoat applied to aluminum, water-thinnable epoxy primer with a CARC urethane topcoat on aluminum, and epoxy polyamide primer with an epoxy polyamide topcoat on both aluminum and steel. Table 1 lists the coatings systems by specification, resin type, and substrate material.

Candidate replacement strippers were solicited from industry and were previewed for probable success before inclusion in the test program. (Organic strippers may contain any or all the following materials: (1) primary solvents, (2) cosolvents, (3) activators, (4) retarders, and (5) surfactants.)

MS-111, which conforms to Mil-R-46116 (now cancelled), is a stripper which contains methylene chloride, phenol, and formic acid. It was included in this study as a control against which alternatives would be measured. Only one of the alternative strippers evaluated contains methylene chloride or phenol, both of which are TTO contributors. Common solvents in the other alternative strippers include 2-(2-butoxyethoxy) ethanol, n-methyl-2-pyrrolidone, monoethanolamine, and aromatic hydrocarbon solvents.



Table 1. Coating Systems Selected for Study

Designation	Specification for:		Coating Type	Substrate Material
	Primer	Topcoat		
A	TT-P-1757	TT-E-489	Zinc-chromate/ Alkyd	Aluminum
B	MIL-P-24441, Formula 150	MIL-P-24441, Formula 152	Epoxy Polyamide/ Epoxy Polyamide	Aluminum
C	MIL-P-53030	MIL-P-53039	Water Thinned Epoxy/ CARC Urethane	Aluminum
D	MIL-P-24441, Formula 150	MIL-P-24441, Formula 152	Epoxy Polyamide/ Epoxy Polyamide	Steel

PROCEDURES AND METHODS

Stripper Performance

Steel and aluminum stock panels were cut into 2 by 3 inch coupons with a 0.25 inch hole drilled on center and 0.5 inch from one end. Cleaned panels were coated on one side at the manufacturers' recommended dry film thickness using conventional air atomization equipment. Dried test panels were aged for 30 days at 105 degrees F in a drying cabinet.

The laboratory evaluation of stripping performance was based on a laboratory-scale mockup of a typical stripping process. Steps in the test were immersion in stripper, caustic dip for acidic strippers, water rinse, and steam cleaning. Thirty-two strippers were evaluated for stripping efficiency under controlled conditions with the four coating/substrate combinations. Manufacturers' recommendations for optimal operational conditions were followed. Stripping parameters are listed in Table 3. Strippers were evaluated for percentage of coating removed for each paint system at specific time intervals.

Alternative strippers which performed adequately in the laboratory tests were evaluated in a 25-gallon pilot test using depot parts rather than test coupons. Stripping temperatures and dilution ratios with water were the same as in the laboratory tests.

Alternative strippers performing successfully in the pilot scale evaluation were considered for full scale production use. Full scale evaluation was performed during normal production operations at SAAD in a 1500 gallon tank. Qualitative results as

well as periodic quantitative coupon analysis were reported. Quantitative coupon analysis was conducted employing prepared specimens similar to those used in laboratory evaluations.

Environmental, Health, and Safety Evaluation

After criteria for evaluation of environmental, health, and safety acceptability were selected, we developed a procedure to assign numerical ratings to permit a quantitative comparison of the hazards associated with each stripper. Each criterion was scored for each component of the stripper. A total weighted average score for the total stripper mixture was calculated by summing the result of the score for each component times the percent of that component in the stripper. A total score for each stripper was determined by summing characteristic scores. In addition, in order to evaluate the potential impact of a particularly hazardous component, a worst case hazard score was calculated for each stripper by summing the highest score for a component in each hazard category.

Several existing scoring procedures for individual criteria (toxicity, bioaccumulation, flammability, reactivity) were used (1,2,3,4,5,6). The scores for individual characteristics were on scales of 0 to 3 with 0 representing no hazard and 3 representing the greatest hazard. If a score were reported in the literature for a criterion for a stripper component, that score was used. In other cases, the same procedure was used to assign a score. If data for assigning a score were lacking, the values were calculated if possible.

RESULTS AND DISCUSSION

Stripper Performance

Table 2 lists the results of the laboratory analyses of the 32 alternative paint strippers. Five of the alternative strippers removed all four coating systems in the laboratory tests. Eight other products removed three of the coating systems and partially removed the fourth in the required 2-hour limit.

Temperature plays a clear role in the paint stripping process. In general, paint removal is more rapid and complete at higher stripping temperatures. Excluding the two chlorinated materials tested, the average stripping temperature for the 31 alternates was 75.2°C. The average test temperature of the four best Phase I alternates was 82.0°C and for the remaining 27 products it was 74.2°C. The average test temperature of the best 12 products was 83.75°C and for the other 19 products it was 69.8°C. It should be noted that all products were evaluated at the highest temperature recommended by the manufacturers. The maximum operating temperature is dependent on the product's flash point. Materials with higher flash points may be used at higher

temperatures. Manufacturers' maximum allowed temperature recommendations were assumed to be acceptable from the standpoint of allowing an appropriate safety margin between operating temperature and flash point.

Three of the four best non-chlorinated alternative paint strippers are alkaline solutions containing monoethanolamine and M-Pyrol. Four other strippers contain both of these chemicals. Three of these materials exhibited significant activity against each of the test coatings. The fourth material was evaluated at a much lower temperature than the other M-Pyrol/monoethanolamine products. Generally these materials remove the coating systems in the order A, D, B, C. This is in contrast to the order for the entire group of strippers evaluated, which is A, D, C, B. Strippers containing primarily M-Pyrol and monoethanolamine appear to be superior to other formulations. Furthermore, on average they remove the epoxy polyamide system more readily than the CARC system. This is significant in that epoxy coatings as a class are generally the most difficult to remove.

Eight of the twelve most successful strippers of known composition have basic pHs. The remaining four are acidic. In general, basic strippers have better substrate compatibility, provided they are not so caustic that they dissolve the metal. Most users are concerned that acidic paint strippers will cause hydrogen embrittlement of both steel and aluminum substrate materials. This is a valid concern especially for aircraft maintenance facilities. Basic strippers pose a smaller risk of metal embrittlement. Users concerned with the effects of embrittlement should conduct tests to determine the safety of any stripping material. Many specifications for paint strippers contain embrittlement testing requirements.

The strippers evaluated in the pilot scale tests at SAAD were McGean-Rohco Cee Bee A-477, Fine Organics F.O. 606, Oakite ALM, Patclin 103B, Patclin 104C, and Turco 5668. It should be noted that laboratory, pilot, and production scale tests overlapped to a certain degree. The materials evaluated in subsequent phases were judged relative to all the materials tested up to that time. In some cases materials with good performance were not evaluated in pilot-scale and production-scale tests while lesser products were.

Table 3 summarizes the results of the pilot scale tests. All the strippers evaluated in pilot scale tests at SAAD except for Patclin 103B performed at a level consistent with laboratory test results. A GC-MS analysis indicated the presence of chloracetic acid in Patclin 104C. This Patclin product contains glycolic acid which is made by reacting NaOH with chloracetic acid. Incomplete conversion may have been the cause of the unacceptable chloracetic acid found in the stripper. Further consideration of Patclin 104C was withdrawn because of the chloracetic acid content. The remaining four strippers were considered to be candidates for full-scale production tests.

Table 2: Operating Parameters and Laboratory Test Results

Stripper	Stripping Temperature	0.5 hr	1.0 hr	1.5 hr	2.0 hr
MS-111	Ambient	ABCD*			
F.O. 606	82 C	ABCD			
Patclin 104C (1:1 with water)	82 C	ABC	ABCD		
Turco 5668	82 C		AD	ABCD	
Cee Bee A-477	82 C	A	A	ABD	ABCD
Enthone S-26	Ambient	AC	AC	AC	ABCD
Enthone S-26 (1:4 with water)	Ambient	A	AD	AD	ABCD
Enthone S-26 (1:9 with water)	Ambient	A	AC	ACD	ACD B=95%
Patclin 126	88 C	CD	CD	ACD	ACD B=50%
Patclin 106Q	82 C	AD	AD	ACD	ACD B=20%
Intex 8798	82 C	A	ACD	ACD	ACD B=85%
Patclin 103B (1:3 with water)	82 C	AD	AD	AD	ACD B=65%
Ardrox 2302	71 C	AC	AC	AC	ACD B=50%
Patclin 125	82 C	D	AD	AD	ACD B=65%
Ardrox 5300-W	82 C	A	A	AD	ACD B=50%
Oakite ALM	82 C	A	A	A	ABD C=35%
Eldorado HT-2230	82 C	A	A	A	ACD
EZE 570-81	71 C	AD	AD	AD	AD C=30%
Omega R-824	71 C	A	A	AD	AD B=90% C=80%
Pentone R-3936	82 C	A	A	AD	AD C=5%

Pavco Decoater 3400	82 C	A	AD	AD	AD
Enthone S-26 (1:19 with water)	Ambient				AD B=40% C=20%
SafeStrip-66	54 C	A	A	A	AD B=10% C=15%
Chem-Lube X-177	93 C	D	D	AD	AD
Chemical Solvents SP-825	88 C		A	A	AD
Chem-Lube XH-36	93 C	D	D	D	D A=40% B=60% C=55%
Chemical Solvents SP-MNP	82 C	A	A	A	A D=90%
Key Chemical 570	79 C	A	A	A	A
NonMeth 120	49 C	A	A	A	A
NonMeth 140	49 C	A	A	A	A
Pavco Decoater 3321	82 C	A	A	A	A
Turco 5555-B	71 C	A	A	A	A
NonMeth 161	Ambient			A	A
Envirosolv L	Ambient				A=50%
Brulin Safety Strip 1000	Ambient				A=30%
Brulin Non-Chlorinated	82 C				

*A: zinc-chromate/alkyd (aluminum); B: epoxy polyamide/epoxy polyamide (aluminum); C: water thinnable epoxy/ CARC urethane (aluminum); D: epoxy polyamide/epoxy polyamide (steel).

Table 3: Pilot Scale Test Results

	Patchlin 104C	Patchlin 103B	Oakite ALM	Cee Bee A-477	Turco 5668	F.O. 606
Blasted Steel CARC	7	6	7	9	6	9
Blasted Steel Epoxy	10	8	10	10	6	8
Phosphate Steel CARC	8	9	10	10	10	10
Conversion Aluminum CARC	8	7	10	10	10	10
Steel Lacquer	10	7	7	9	10	9
Steel and Aluminum Alkyd	9	9	10	10	10	10
Conversion Aluminum Latex	7	7	10	10	10	10
Total	59	53	64	68	62	66

10 = 0 - 0.5 hours
 9 = 0.5 - 1 hours
 8 = 1 - 1.5 hours
 7 = 1.5 - 2 hours
 6 = 2+ hours

Environmental, Health, and Safety Evaluations

The results of the ratings of the most promising candidate strippers compared to MS-111 for environmental, health, and safety hazard criteria are shown in Table 4. A higher score indicates a relatively greater risk for both individual criteria and total stripper hazard. These ratings are based on available data from Material Safety Data Sheets and published sources. The use of existing data to rate the expected environmental hazard of paint strippers allows calculation of an estimate of hazard with

Table 4. Paint Stripper Hazard Summary*

	<u>MS-111</u>	<u>Oakite</u> <u>ALM</u>	<u>Pat. 103</u>	<u>Pat. 104</u>	<u>F.O. 606</u>	<u>C.B.</u> <u>A-477</u>	<u>Turco</u> <u>5668</u>
T O X I C I T Y	HUMAN TOXICITY						
	2.2	2.3	2.2	1.9	2.1	2.6	2.3
	ACUTE ENVIRONMENTAL						
	1.1	0.8	0.9	1.1	0.6	0.8	0.6
	CHRONIC ENVIRONMENTAL						
	2.1	2.1	2.3	1.8	1.9	2.0	1.6
E N V I R O N M E N T A L	BIOACCUMULATION						
	0.1	0	0.2	0.2	0	0	0
	PERSISTENCE						
	2.5	0.4	0.3	0.5	0.7	0.5	0.2
	ENVIRONMENTAL TRANSPORT						
	2.9	2.0	2.1	1.9	1.8	1.6	1.4
S A F E T Y	CORROSIVITY OF STRIPPER						
	3.0	1.7	1.6	1.7	2.7	2.8	2.4
	REACTIVITY OF STRIPPER						
	1.2	0.8	1.5	1.2	0.2	0.5	0.4
	IGNITABILITY						
	1.2	1.6	1.8	1.2	1.1	1.4	1.5
	16.3	11.7	12.9	10.8	11.1	12.2	10.4

* = a higher score indicates greater hazard

a minimal investment of funds and time. A shortcoming of this approach is that some or most data are missing for some compounds. As a result, a score is assigned which is based on available data only and may not be totally representative for the stripper mixture.

Table 5 lists the order of relative hazard for the alternative strippers based on weighted average and worst case scores. The total weighted average scores show that any of the six candidate strippers are less hazardous than MS-111. Based on these calculations, Turco 5668 appears to be slightly preferable from an environmental and safety hazard point of view. However, data are not available for the petroleum distillate in Turco 5668. Although the raw material supplier apparently intends to limit the distillate to aliphatic hydrocarbon compounds, it is not clear what compounds are actually present or what contaminant hydrocarbons may be included. Based on experience with another stripper, there is concern that this stripper may contain some more environmentally hazardous aromatic hydrocarbon compounds. If hazardous hydrocarbons are present, this stripper should have a less favorable rating.

Table 5. Total Stripper Hazard Scores from Worst to Best

Weighted Average	Worst Case
MS-111 ----- 16.3	MS-111, ALM ----- 22.0
Patclin 103 --- 12.9	
Cee Bee A-477 - 12.2	Patclin 103, 104 - 19.5
ALM ----- 11.7	
Patclin 104 --- 11.5	Turco ----- 17.0
F.O 606 ----- 11.1	
Turco 5668 ---- 10.4	Cee Bee, F.O. 606 -- 16.0

In addition to the hazard scores, hazardous waste concerns and environmental and health regulations restricting discharges are also more favorable for the candidate strippers compared to MS-111 (Table 6). Five of the six alternative strippers have considerably fewer regulatory restrictions.

Field Tests

Oakite ALM was evaluated in a full-scale field test. Results were disappointing. Depletion of the active components either through evaporation or absorption in the tank led to an early decline in stripping power as shown by excessive stripping time both for production parts and for uniform test coupons. Because of the nature of the production operations at the test site the evaporation rate was above an acceptable level. The manufacturer analyzed the depleted stripper and provided a

Table 6. Regulatory Restrictions Affecting Strippers

General Disposal Concerns			Specific Regulations Which Apply					Environmental Concerns		Health*
	Number of Components Regulated/1	Hazardous Waste Concerns/2	Wastewater Effluent Concerns/3	TSCA	RCRA	CERCLA	CWA	CAA	FIFRA	OSHA NIOSH ACGIH
MS-111	4/4	10	7	X	X	X	X	X	X	5 ppm
Oakite ALM	10/10	6	7	X	X	X	X	X	X	0.2 ppm
Patclin 103B	3/6	2	3	X			X			3 ppm
Patclin 104C	7/10	3	2	X	X					N.E.
F.O. 606	3/6	3	3	X	X				X	ceiling 3 mg/m ³
C.B. A-477	3/5	2	3	X					X	3 ppm
Turco 5668	4/6	2	4	X		X	X		X	3 ppm

* = Most stringent worker exposure TLV which applies

/1= Number of components regulated/number of components in stripper

/2= Number of concerns out of a possible 10.

/3 = Number of concerns out of a possible 8.

N.E. = None Established

replenishment solution. The replenishment proved to be of marginal help. The full-scale evaluation of Oakite ALM was discontinued after approximately 9 months.

Besides the stripper performance evaluation, environmental monitoring was performed during the field test with Oakite ALM. Results of analyses of stripper and rinse water revealed the presence of a complex mixture of aromatic hydrocarbon compounds in addition to the compounds reported by the manufacturer as components of the stripper. It is not surprising that the manufacturer did not know of the presence of these compounds in their stripper. A petroleum distillate such as was used in ALM is a complex blend of hydrocarbons which is characterized primarily by its boiling range. The identified compounds increase the hazard and decrease the environmental acceptability of the stripper compared to the estimates based on the composition listed by the manufacturer.

F.O. 606 was also evaluated in production-scale tests. The performance of this material over a 14-month period is shown in Table 7. Performance was initially acceptable with strip times of less than 2-hours noted for most production parts. The evaporation rate was significant, and frequent additions of fresh stripper were necessary to maintain a sufficient depth in the tank. Stripper performance declined over the duration of the 12-month test. Significantly longer contact times were needed to remove the same coatings. Epoxy coatings were especially difficult to remove.

CONCLUSIONS AND RECOMMENDATIONS

Four candidate strippers demonstrated performance in laboratory tests consistent with the goals of the study. A total of six strippers were evaluated on a pilot scale. Four of the pilot-scale candidates tested were initially recommended for full-scale production use on an experimental basis. Oakite ALM was evaluated in full-scale production and did not meet the minimum requirements nor did it perform at a level consistent with laboratory and pilot-scale tests. In addition, chemical analyses of ALM stripper and rinse water samples revealed the presence of a complex mixture of aromatic hydrocarbon compounds which pose considerable health and environmental risk. F.O. 606 was also evaluated in production-scale tests. The user indicated initially acceptable performance which declined to marginal as evaporation of the stripper occurred. Material cost was high, especially considering the relatively high evaporation rate. Cee Bee A-477 and Turco 5668 have also been recommended for use on a trial basis.

Table 7: F.O. 606 Field Test Summary

Date	0.5 hr	1.0 hr	1.5 hr	2.0 hr
11/30/89	A	AC	AC	AC B=73%
1/2/90	A	AC	AC	AC B=31%
2/2/90	A	AC	AC	AC B=27%
[2/7/90 >> 140 gallons F.O. 606 added to tank]				
3/2/90	A	AC	AC	AC B=35%
[3/12/90 >> 110 gallons F.O. 606 added to tank]				
3/30/90	A	AC	AC	AC B=56%
[9/90 >> 330 gallons F.O. 606 and 110 gallons NMP added to tank]				
9/14/90	A	A	AC	AC B=59%
10/16/90	A	A	AC	AC B=57%
3/14/91	A	A	A	A B=2% C=33%

A = alkyd on aluminum
 B = epoxy on aluminum
 C = CARC on aluminum

Compared to methylene-chloride based stripper formulations, the alternative strippers evaluated in the pilot scale tests are less hazardous. Also, none of the alternative strippers contribute to TTO discharge. From the hazard scores calculated in this study, however, it is clear that all of the alternative strippers involve some safety and environmental hazards. Selection of alternative strippers at a particular facility or installation requires making a judgment based upon the stripping performance required for the workload and which safety and environmental hazards can be managed best at that facility. Petroleum distillate in paint strippers, e.g., Oakite ALM and Turco 5668, is likely to contain hazardous hydrocarbon compounds, at least as contaminants. For this reason, when other alternative strippers are available with comparable performance, we recommend selecting a stripper which does not contain petroleum distillate.

An example of the need to evaluate a stripper in the context of the particular intended use is the experience of Red River

Army Depot (RRAD) with Turco 5668. The authors of this paper have not conducted a comparable field test to compare that product with the two which have been fully tested. RRAD tried the stripper and found that it was not satisfactory for their equipment and workload.

It is apparent that judgment of what constitutes successful performance of a stripper may depend as much upon what the user is willing to accept, or the individual's criteria, as upon the characteristics of the stripper. For example, SAAD decided that F.O. 606 is not an adequate replacement stripper for their purposes. Naval Aviation Depot Alameda, on the other hand, reports satisfaction with the same stripper. Alameda NADEP, however, accepts stripping times as long as overnight compared to the desired 2-hour maximum at SAAD. The use of methylene chloride-based strippers is not permitted at Alameda NADEP by the local air pollution control district. The choice is not whether to use a methylene chloride-based stripper versus an alternative but whether to use an alternative stripper in the dip tanks or not use dip tanks.

Evaporation and dragout losses are significant for methylene chloride-based cold strippers and for the heated alternatives. Costs for stripper and replenishment solvents are approximately three to four times higher for the alternative strippers compared to methylene chloride-based strippers. However, when the choice is higher stripper cost or elimination of dip tank stripping, it may be less costly to use an alternative chemical stripper. The increasing regulatory burden of using methylene chloride, including the new air toxic restrictions, may also reduce the difference in costs. Engineering controls may need to be installed, and operation and disposal costs may increase for methylene chloride strippers where their use is not prohibited.

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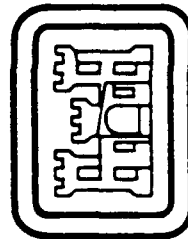
Acknowledgements. The authors wish to acknowledge the contributions of S. Glascock, technician who performed the laboratory stripping performance tests, and P. Hoglund and G. Barrett, research assistants who compiled the environmental, health, and safety data. Assistance from the Sacramento Army Depot during the project's planning, pilot testing, and field testing stages is also appreciated.



EVALUATION OF ALTERNATIVE CHEMICAL PAINT STRIPPERS TO REDUCE TTO DISCHARGES AND MINIMIZE HAZARDOUS WASTE

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BACKGROUND

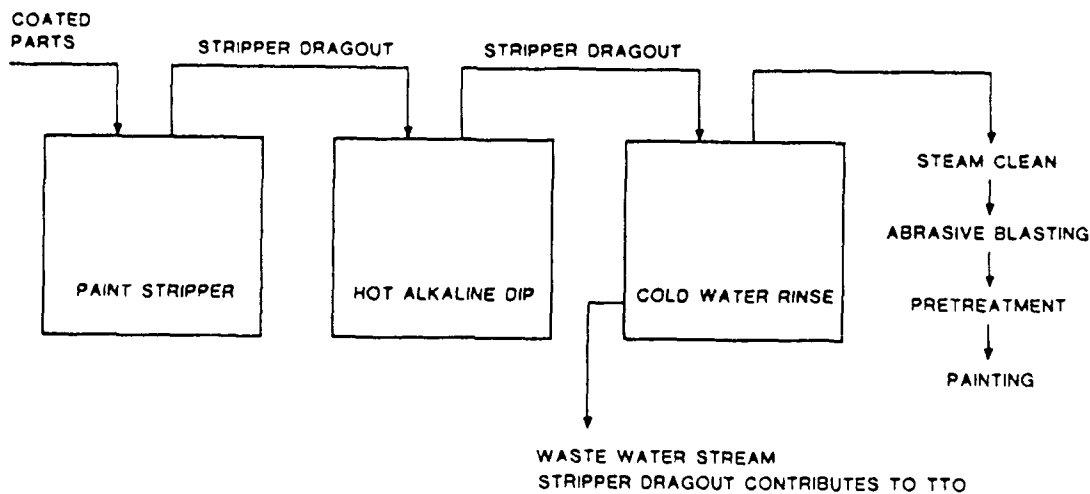
- 1984 U.S. EPA ESTABLISHED 2.13 mg/l MAXIMUM CONCENTRATION FOR TTO
- POPULAR STRIPPERS CONTAIN METHYLENE CHLORIDE AND PHENOL-TTO CONTRIBUTORS
- HAZARDOUS WASTE AND WORKER SAFETY CONSIDERATIONS

OBJECTIVES

- IDENTIFY AND EVALUATE ALTERNATIVE STRIPPERS
- ESTABLISH STRIPPER EFFECTIVENESS AND ENVIRONMENTAL ACCEPTABILITY
- ALLEVIATE TTO COMPLIANCE PROBLEMS
- MINIMIZE ENVIRONMENTAL AND HEALTH RISKS AND DISPOSAL LIABILITIES



METALS REFINISHING PROCESS



REINBOOMING TITOGARD ABC

APPROACH

- STEPWISE EXPERIMENTAL APPROACH
- PHASE I - LABORATORY EVALUATION OF STRIPPING EFFICIENCY
 - HEALTH / HAZARD ANALYSIS
- PHASE II - PILOT SCALE EVALUATION AT SAAD
- PHASE III - PRODUCTION LEVEL STRIPPING AT SAAD
 - ENVIRONMENTAL SAMPLING AND EVALUATION



CRITERIA FOR AN ACCEPTABLE PAINT STRIPPER

1. RAPID REMOVAL OF A BROAD SPECTRUM OF COATINGS
2. LOW EVAPORATION RATE
3. EASILY REPLENISHED
4. NO TTO CHEMICALS
5. ENVIRONMENTALLY ACCEPTABLE, SAFE TO USE AND RELATIVELY EASY TO DISPOSE
6. COMMERCIALY AVAILABLE

LABORATORY STRIPPER TESTING

- LABORATORY SCALE MOCKUP OF SAAD
- 2 x 3 INCH COATED ALUMINUM & STEEL PANELS
- ACCELERATED AGING OF TEST SAMPLES
- STRIPPING EVALUATED FOR DIP PERIODS OF UP TO 3 HOURS
- MEASURE OF PERCENT OF COATING STRIPPED
- MOST EFFICIENT CANDIDATES IDENTIFIED

COATING SYSTEMS

COATING	SUBSTRATE
A = ZINC-CHROMATE / ALKYD	ALUMINUM
B = EPOXY POLYAMIDE/EPOXY POLYAMIDE	ALUMINUM
C = EPOXY / POLYURETHANE CARC	ALUMINUM
D = EPOXY POLYAMIDE/EPOXY POLYAMIDE	STEEL

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RESULTS OF LABORATORY STRIPPER TESTING: ACCEPTABLE STRIPPERS

STRIPPER	HEATED	HOT CAUSTIC DIP	COATING SYSTEMS REMOVED 2 HR
MS-111 (CONTROL)	NO	YES	ABCD*
FINE ORGANIC 606	YES	NO	ABCD*
PATCLIN 104C	YES	NO	ABCD**
TURCO 5668	YES	NO	ABCD***
McGLEAN-ROHCO CEE BEE A-477	YES	NO	ABCD

* REMOVED IN 0.5 HR.
 ** REMOVED IN 1.0 HR
 *** REMOVED IN 1.5 HR

RESULTS OF LABORATORY STRIPPER TESTING: ACCEPTABLE STRIPPERS,

(CONTINUED)

STRIPPER	HEATED	HOT CAUSTIC DIP	COATING SYSTEMS REMOVED (2HR)
PATCLIN 126	YES	NO	ACD (B = 50%)
PATCLIN 106Q	YES	NO	ACD (B = 20%)
INTEX 8798	YES	NO	ACD (B = 85%)
PATCLIN 103B	YES	NO	ACD (B = 65%)
ARDROX 2302	YES	NO	ACD (B = 50%)
PATCLIN 125	YES	NO	ACD (B = 65%)
ARDROX 5300-W	YES	NO	ACD (B = 50%)
OAKITE ALM	YES	NO	ABD (C = 35%)

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ENVIRONMENTAL HAZARD ASSESSMENT CRITERIA

- TOXICITY / SAFETY AND ENVIRONMENTAL FATE
- USE FACTORS
- REGULATIONS

TOXICITY, SAFETY, AND ENVIRONMENTAL FATE

- TOXICITY
 - HUMAN
 - ACUTE ENVIRONMENTAL
 - CHRONIC ENVIRONMENTAL
- ENVIRONMENTAL FATE
 - PERSISTENCE
 - BIOACCUMULATION
 - TRANSPORT
- SAFETY
 - CORROSIVITY
 - REACTIVITY
 - IGNITABILITY

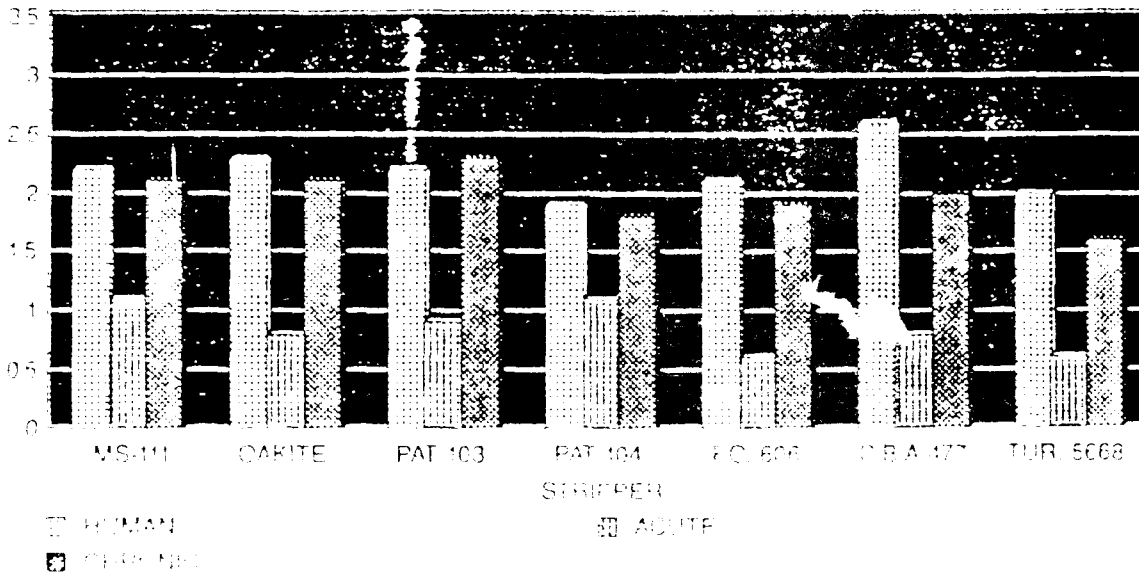
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USE FACTORS

- VOLUME OF STRIPPER USED
- EVAPORATION
- TEMPERATURE
- DILUTION WITH WATER

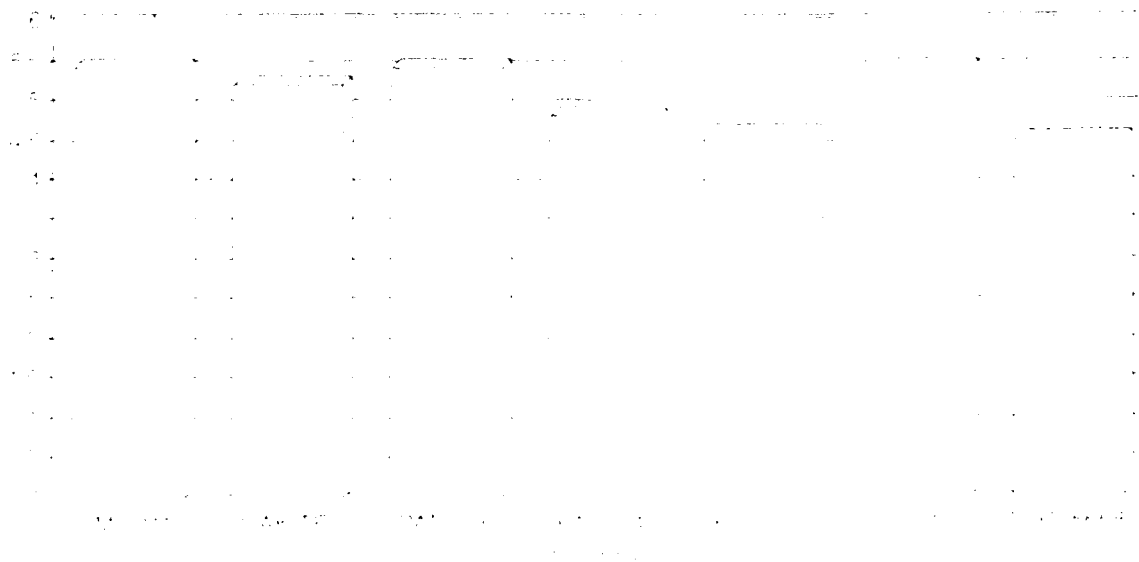
PAINT STRIPPER HAZARD TOXICITY

TOXICITY

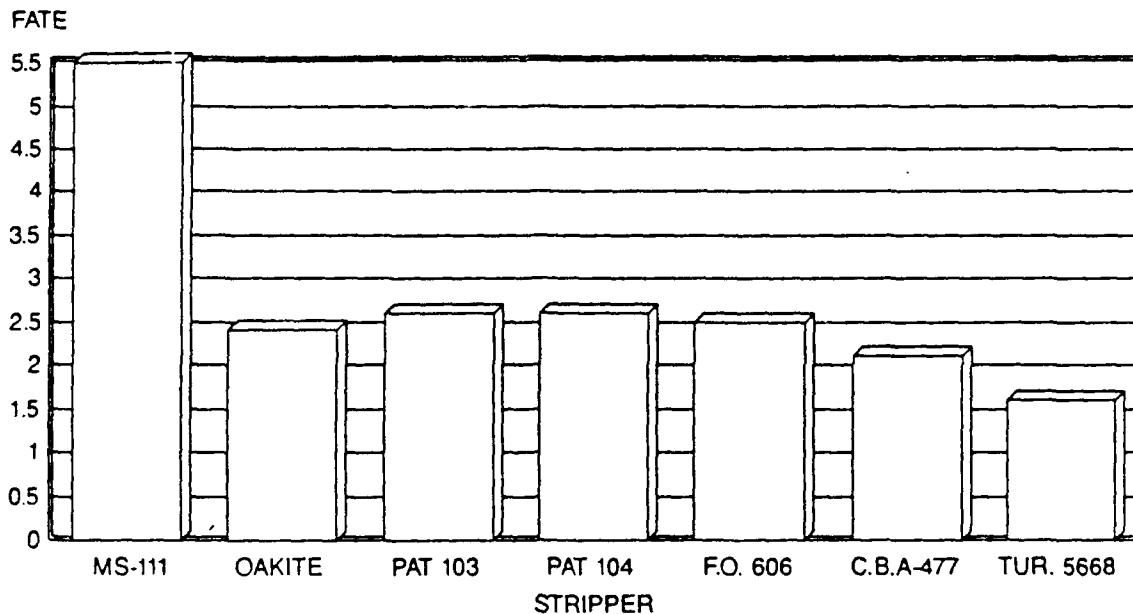


PAINT STRIPPER HAZARD TOXICITY SUMMARY

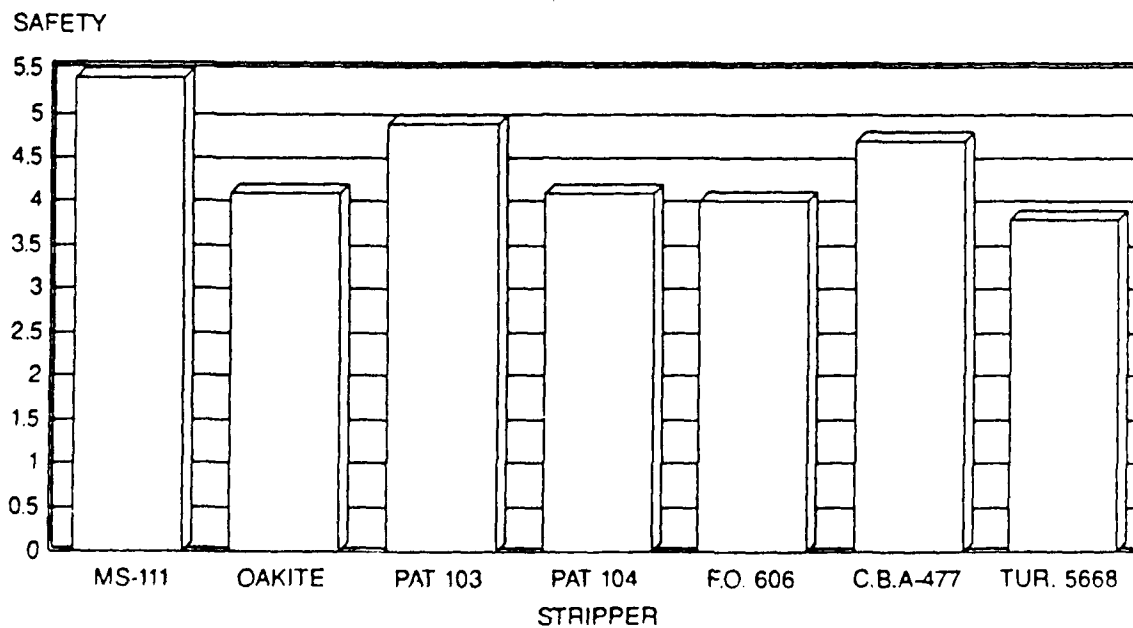
TOXICITY



PAINT STRIPPER HAZARD ENVIRONMENTAL FATE SUMMARY

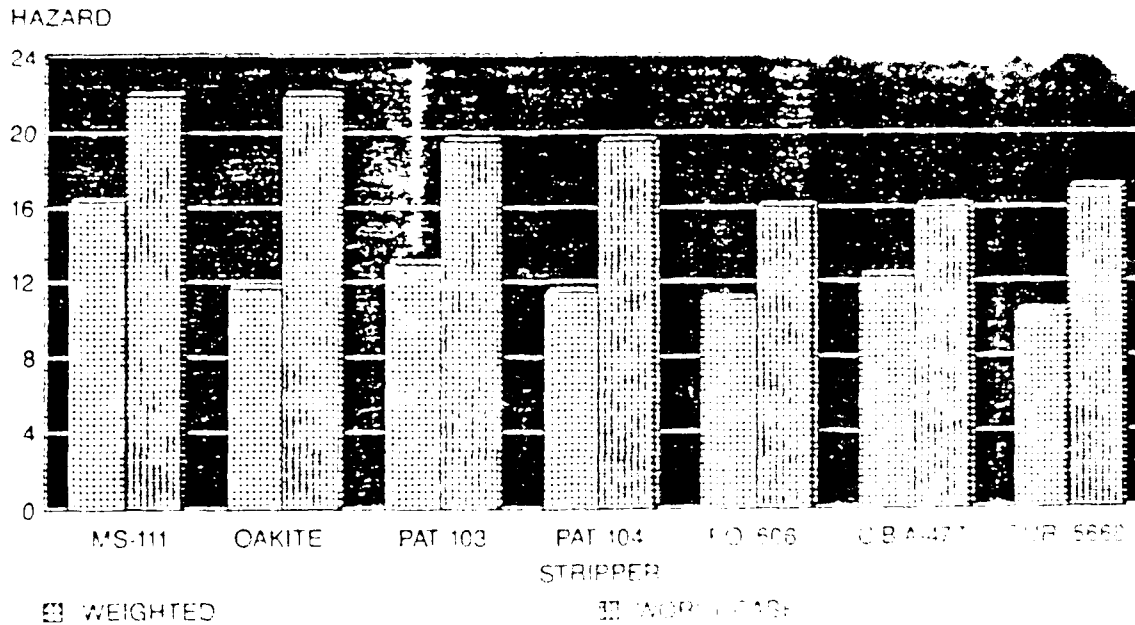


PAINT STRIPPER HAZARD SAFETY SUMMARY



STRIPPER HAZARD SCORES

TOTAL HAZARD



REGULATORY RESTRICTIONS

	NO COMP	HAZ WASTE (C)	WASTE WATER EFF (R)	OSHA NIOSH	RCRA	RTCA	DEVELO	CAA	CAA	EIP
MS-111	4/4	10	7	5/10	X	X	X	X	X	X
OAKITE ALM	10/10	6	7	11/11	X	X			X	X
PATCLIN 103	3/6	2	3	3/10	X			X		
PATCLIN 104	7/10	3	2	N.E.	X	X				
F.O. 606	3/6	3	3	3/10	X	X				X
C.B. A-477	3/5	2	2	3/10	X					X
TURCO 5668	4/6	2	4	3/10	X		X	X	X	X

RESULTS OF FIELD TEST AT SAAD

- OAKITE ALM PERFORMANCE NOT SATISFACTORY
 - EVAPORATION
 - LOSS OF STRIPPING EFFICIENCY
 - ENVIRONMENTAL HAZARD

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RESULTS OF FIELD TEST AT SAAD

- F0-606
 - EVAPORATION
 - PERFORMANCE ACCEPTABLE TO MARGINAL



SUMMARY RESULTS OF STRIPPER EVALUATION

- PHASE I: 32 CANDIDATES EVALUATED
- PHASE II: 6 CANDIDATES EVALUATED
4 RECOMMENDED FOR PHASE III
- PHASE III: 2 CANDIDATES EVALUATED
2 CANDIDATES RECOMMENDED FOR
EVALUATION

reinb027 n08 6/19/91 BLK

EVALUATION OF ALTERNATIVE STRIPPERS COMPARED TO MeCl

- NO TTO CONTRIBUTORS
- LESS HAZARDOUS
- SLOWER STRIPPING FOR SOME COATINGS
- HIGHER MATERIAL COST



GUIDELINES FOR SELECTION OF STRIPPERS

- HAZARDS
 - ALTERNATIVES LESS THAN MeCl STRIPPERS
 - ALTERNATIVES NOT HAZARD FREE
 - AVOID PETROLEUM DISTILLATE IF OTHER ALTERNATIVES

reimb029 n08 6/19/91 BLK

GUIDELINES FOR SELECTION OF STRIPPERS

(CONTINUED)

- TRADEOFFS
 - STRIPPER PERFORMANCE REQUIRED
 - TYPES OF HAZARDS CAN MANAGE BEST

GUIDELINES FOR SELECTION OF STRIPPERS

(CONTINUED)

- ACCEPTABILITY
 - HIGHER PURCHASE COST FOR ALTERNATIVES VERSUS LIFE CYCLE COSTS (DISPOSAL AND CONTROLS)
 - SLOWER STRIPPING VERSUS ELIMINATION OF DIP TANK STRIPPING (ALAMEDA NADEP)

reimb031 n08 6/19/91 BLK

GUIDELINES FOR SELECTION OF STRIPPERS

(CONTINUED)

- NUMBER OF STRIPPERS
 - SINGLE REPLACEMENT MAY NOT BE ADEQUATE
 - CONSIDER LESS HAZARDOUS ALTERNATIVE FOR MOST COATINGS
 - MAY NEED DIFFERENT ALTERNATIVE FOR COATINGS HARDEST TO STRIP



RECOMMENDED STRIPPERS

THE FOLLOWING STRIPPERS ARE RECOMMENDED FOR USE ON AN EXPERIMENTAL BASIS FOR REMOVAL OF A BROAD RANGE OF COATINGS FROM METALLIC SUBSTRATES:

1. FINE ORGANICS FO-606
2. McGEAN ROHCO CEE-BEE A-477

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COMMONALITIES OF RECOMMENDED STRIPPERS

- ALKALINE
- SIMILAR FORMULATIONS
- ELEVATED TEMPERATURE
- SUPPLIER SUPPORT INCLUDING ESTABLISHED PROCEDURES FOR TESTING STRIPPER DEPLETION
- TWO-PHASE WITH OIL SEAL TO REDUCE EVAPORATION



CONCLUSIONS

- SUCCESSFUL ALTERNATIVE CHEMICAL PAINT STRIPPERS IDENTIFIED IN PILOT TESTS
- MORE DEMONSTRATIONS NEEDED IN PRODUCTION SCALE TESTS
- SELECTION BASED ON PERFORMANCE REQUIREMENTS AND HAZARD MANAGEMENT
- ACCEPT SOME CHANGE IN REQUIREMENTS
- MORE THAN ONE ALTERNATIVE STRIPPER MAY BE REQUIRED





EVALUATION OF THE IMPACT OF THE NEW TOXICITY
CHARACTERISTIC RULE ON ARMY WASTE STREAMS

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ABSTRACT

The impact of the new Resource Conservation and Recovery Act (RCRA) Toxicity Characteristic (TC) Rule on the management of the Army's solid and hazardous wastes was assessed. The new TC Rule, which became effective on 25 September 1990, replaces the Extraction Procedure (EP) Toxicity method with the Toxicity Characteristic Leaching Procedure (TCLP). The new TC Rule increases the number of toxic constituents from 14 to 39. When any of these toxic constituents are present, above a regulatory threshold concentration, in the leachate from the TCLP on a specific waste, the waste must be managed in accordance with RCRA regulations. Waste streams that were assessed include the following: Unserviceable military ammunition that is U.S. Department of Transportation (DOT) "Class C", classified as Department of Defense (DOD) Quantity-Distance Hazardous Classification "1.4", and small arms ball ammunition of calibers up to and including 0.50; pentachlorophenol (PCP) and creosote treated wood products (e.g., ammunition boxes, pallets, and railroad ties); used oil and soil, water, and other debris contaminated by oil or other petroleum products; batteries (e.g., magnesium, lithium-sulfur dioxide, lithium-thionyl chloride and alkaline); wastewaters; waste from painting operations; and polychlorinated biphenyls (PCBs) and PCB contaminated waste. Data, generated by the DOD community and the commercial sector, are presented for a number of waste streams. The data indicates that some small arms ammunition, previously considered exempt from RCRA management, are likely to be hazardous waste under the TC Rule. The management of some wastewaters may also be significantly impacted by the TC Rule.



EVALUATION OF THE IMPACT OF THE NEW TOXICITY CHARACTERISTIC RULE ON ARMY WASTE STREAMS

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Introduction.

On March 29, 1990, the U.S. Environmental Protection Agency (EPA) promulgated the Toxicity Characteristic final rule¹. This rule replaced the hazardous waste characteristic of Extraction Procedure Toxicity (EP TOX) with a new Toxicity Characteristic (TC). Essentially, the new TC differed from the EP TOX in three major areas:

The rule added 25 new organic compounds to the list of the 14 constituents (8 metals, 4 insecticides, and 2 herbicides) previously regulated under the EP TOX that may render a waste hazardous.

It established regulatory thresholds or levels for the new constituents. Any solid waste capable of leaching one or more of these organic constituents in concentrations greater than specified levels would be regulated as a hazardous waste. A list of these constituents and their regulatory levels is shown as Table 1.

The rule also replaced the extraction procedure (EP) with the toxicity characteristic leaching procedure (TCLP) as the means for determining if a waste exhibits a toxic characteristic.

Detailed procedures to perform the TCLP in the laboratory are contained in Appendix II of 40 Code of Federal Regulations (CFR) Part 261². Furthermore, the TCLP has been designated as EPA Method 1311, and will be incorporated into the next edition of Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846³. A summary of the significant differences between the TCLP and EP methods include the following:

The TCLP uses a more aggressive leaching or extraction fluid which could result in higher metal concentrations than would be obtained for the same sample using the EP.

The TCLP requires that solid wastes (i.e., those containing greater than or equal to 0.5 percent solids) undergo a particle size reduction unless the solid has a surface area equal to or greater than 3.1 cm²/gm, or is capable of

TABLE 1. TOXICITY CHARACTERISTIC CONSTITUENTS.

CONSTITUENT	EPA HAZARDOUS WASTE NUMBER	REGULATORY LEVEL(mg/L)
METALS		
Arsenic	D004	5.0
Barium	D005	100.0
Cadmium	D006	1.0
Chromium	D007	5.0
Lead	D008	5.0
Mercury	D009	0.2
Selenium	D010	1.0
Silver	D011	5.0
VOLATILES		
Benzene	D018	0.5
Carbon tetrachloride	D019	0.5
Chlorobenzene	D021	100.0
Chloroform	D022	6.0
1,2-Dichloroethane	D028	0.5
1,1-Dichloroethylene	D029	0.7
Methyl ethyl ketone	D035	200.0
Tetrachloroethylene	D039	0.7
Trichloroethylene	D040	0.5
SEMIVOLATILES		
Vinyl chloride	D043	0.2
o-Cresol *	D023	200.0
m-Cresol *	D024	200.0
p-Cresol *	D025	200.0
Cresol	D026	200.0
1,4-Dichlorobenzene	D027	7.5
2,4-Dinitrotoluene	D030	0.13
Hexachlorobenzene	D032	0.13
Hexachloro-1,3-butadiene	D033	0.5
Hexachloroethane	D034	3.0
Nitrobenzene	D036	2.0
Pentachlorophenol	D037	100.0
Pyridine	D038	5.0
2,4,5-Trichlorophenol	D041	400.0
2,4,6-Trichlorophenol	D042	2.0
* If o-,m-,and p-Cresol can not be differentiated, total is used.		

TABLE 1. TOXICITY CHARACTERISTIC CONSTITUENTS (CONTINUED).

CONSTITUENT	EPA HAZARDOUS WASTE NUMBER	REGULATORY LEVEL(mg/L)
PESTICIDES/HERBICIDES		
Chlordane	D020	0.03
2,4-D	D016	10.0
Endrin	D012	0.02
Heptachlor(& its Epoxide)	D031	0.008
Lindane	D013	0.4
Methoxychlor	D014	10.0
Toxaphene	D015	0.5
2,4,5-TP (Silvex)	D017	1.0

passing through a 9.5 mm standard sieve. This could result in higher extract contamination.

The TCLP increases filtration pore size which may allow greater amounts of particulates and consequently contaminants to be extracted.

The TCLP incorporates stringent quality assurance/quality control (QA/QC) requirements including sample holding times. The EP had minimal QA/QC requirements.

The TCLP expands the number of constituents from 14 to 39. A separate extraction procedure is required for volatile organic constituents using a zero-headspace extractor.

The cost to perform the TCLP is estimated to be two to three times more than it is to perform the EP.

IMPACTS ON ARMY WASTES STREAMS.

Because of the changes listed above, significant impacts will result from the expanded list of constituents and the more aggressive leaching procedure. Particular emphasis will have to be placed on a generator's Waste Analysis Plan. This Plan will not only have to include hazardous wastes resulting from the new organic compounds which have to be considered, but it will also have to be updated to address wastes that may not have been hazardous by the EP TOX method, but will be under TCLP. Waste generators should obtain as much information as possible on their

waste streams.. This information may be available from Material Safety Data Sheets (MSDSs) for chemical formulations or by contacting applicable manufacturers. Ideally, enough information can be acquired to make a decision on whether a waste is hazardous without performing a costly TCLP. If adequate information is not available to eliminate the need for the TCLP, the generator may still be able to minimize the number of test constituents.

In an effort to anticipate some of the more immediate impacts on the Army resulting from this regulatory change, several waste streams were assessed with respect to the TCLP⁴. The results of this assessment is as follows:

(1) Small Arms Ammunition (Class C). In the past, unserviceable military ammunition that is DOT "Class C", classified as DOD Quantity-Distance Hazardous Classification "1.4", and is small arms ball ammunition of calibers up to and including 0.50 has not been considered reactive within the meaning of 40 CFR Subpart 261.23, and as such has been managed as non-HW by the Army. This unserviceable ammunition is typically treated in a deactivation/popping furnace or at an open burning/open detonation ground. Based on theoretical solubility calculations using type and composition of various small arms ammunition, it is very likely that several formulations will result in HW because of 2,4-DNT (and perhaps barium and lead leachate concentrations as well). In order to confirm such calculations, however, it will be necessary to perform the TCLP on selected small arms ammunition to verify this assumption.

(2) Used Oil. There should be no significant impact from the TC rule on used oil management. Used oil that exhibits any of the Hw characteristics and is recycled through burning for energy recovery or rerefined is still regulated in accordance with 40 CFR 261.6 and 266.40. The TC rule could impact used oil that is not recycled, and soil, water and debris contaminated by used oil. The TC contaminants, other than heavy metals, that might be present in properly segregated used oil are benzene and cresols (i.e., components often present in virgin oil products). These compounds might also be present in contaminated soil, water, and debris resulting from spills of other petroleum products (e.g., gasoline, fuel oil, diesel fuel, and jet fuel). It should be noted that the EPA has deferred, as HW, petroleum contaminated groundwater, soils, and debris that are associated with corrective action activities for underground storage tank leaks.

(3) Pentachlorophenol (PCP) Treated Wood. Several studies were reviewed that had actually tested PCP-treated wood using the TCLP^{5,6,7}. In general, all of the TCLP data fell below 15 mg/L. Comparing this information to the present TCLP concentration limit of 100 mg/L, it can be concluded that PCP-



treated wood is not a HW. However, the EPA is currently reviewing the TCLP concentration limit of 100 mg/L. The intent of the review is to determine if the limit should be lowered, and if so, to what extent. A reevaluation of the HW status of PCP-treated wood might be required based upon future EPA decisions.

(4) Creosote treated Wood. Utility poles and railroad ties are often treated with creosote. While data on TCLP concentrations for creosote-treated wood have not been identified within the DOD, data collected within the private sector indicates that creosote-treated wood does not exhibit the TC⁸.

(5) Paint Wastes. Paint formulations, although they vary greatly in composition, may contain heavy metal and organic TCLP constituents. Saturated paint exhaust filters, water curtain wastewaters and sludges, spent thinners, and unusable excess paint are typical paint wastes that may be impacted by the TC rule. Painting operations may be able to minimize this impact by integrating pollution prevention practices into the process, or by using knowledge of the composition of paints and thinners to reduce the amount of testing required.

(6) Batteries. There are numerous battery types in use within the Army, each with its own unique electrochemistry and composition. Since it is virtually impossible to predict the impact of the TCLP on each of these items, study was initiated by U.S. Army Communications-Electronics Command (CECOM) to address these issues⁹. As of this date, no results are available.

(7) Wastewater Impoundments. Surface impoundments that currently treat or contain wastewaters previously not subjected to RCRA requirements may now be regulated if concentrations of organic constituents in the wastewater exceed TC regulatory limits. The wastewater and spent solvent mixture exemption contained in 40 CFR 261.3 does not apply to wastewaters that exhibit a HW characteristic. Therefore, newly regulated impoundments will be subject to RCRA permitting conditions and must meet minimum technology requirements (i.e., install liners and a leachate collection system) by March 29, 1994. However, installations may choose to replace surface impoundments with wastewater tanks which will be less costly than retrofitting surface impoundments, and while not exempt from HW management standards under 40 CFR 264.1 and 265.1 are easier to operate in compliant status.

(8) Polychlorinated Biphenyl (PCB) Waste. The EPA has specifically exempted PCB-containing dielectric fluids removed from electrical transformers, capacitors, and associated PCB-contaminated electrical equipment from the TC rule. These wastes may exhibit the TC, not because of containing PCBs, which are not on the TC list, but because they may contain other TC constituents such as chlorinated benzenes. Other PCB-containing

wastes that are hazardous (i.e., listed or exhibit a HW characteristic including the existing EP TOX wastes D004-D017) are still subject to the HW regulations.

NEED FOR ADDITIONAL INVESTIGATION.

As alluded to above, there are any number of initiatives that can be undertaken to clearly define HW practices under the TC rule. Among the more obvious measures that should be accomplished are the following:

(1) Initiate a study to perform the TCLP on selected small arms ammunition to verify if 2,4-DNT, barium, and lead (at a minimum) are in fact HW under the TC rule.

(2) Investigate alternative non-TC propellant mixtures.

(3) Investigate alternative non-TC solvents.

(4) Because of its potential monumental impact on Army operations associated with World War II vintage buildings and structures, considerable work has to be done to address HW issues of lead paint chips and lead painted construction debris. Construction debris is particularly important in light of the TCLP requirement for particle size reduction.

(5) Continued efforts need to be expended in order to define the TC implications associated with batteries.

(6) For those waste streams that were just below toxic levels using the EP, it will be necessary to reevaluate these in light of the more aggressive leaching procedures under the TC.

FUTURE IMPACTS.

As we look down the road, what additional requirements might be expected in the years ahead? Here are some issues that will very likely impact on the Army in the near future:

(1) For one thing, it is a foregone conclusion that there will be additional organic chemicals added to the TC list very soon. The following seven constituents were deferred largely because the kinetics of hydrolysis were not well defined-

- acrylonitrile
- bis(2-chloroethyl)ether
- methylene chloride
- 1,1,1,2-tetrachloroethane
- 1,1,2,2-tetrachloroethane
- 1,1,1-trichloroethane

-1,1,2-trichloroethane

Once a conservative estimate of hydrolysis can be made, they will be added to the TC list. Similarly, the following six constituents were deferred because the steady state assumption of the Rule's groundwater model was deemed inappropriate:

- carbon disulfide
- 1,2-dichlorobenzene
- isobutanol
- 2,3,4,6-tetrachlorophenol
- toluene
- phenol

As with the hydrolysis problem, once the steady state issue can be conservatively addressed, these will also be included on the TC list. The sheer volume of usage of chemicals such as toluene, methylene chloride, and 1,1,1-trichloroethane will result in major impacts for industrial and laboratory operations at many Army installations.

(2) Regulatory levels, particularly for the heavy metals, under the TC rule find their basis from maximum contaminant levels (MCLs) multiplied times a dilution attenuation factor (DAF). In most instances the DAF is a factor of 100. Because of the current emphasis on lead in drinking water, there is a distinct possibility that the MCL for lead will probably be lowered¹⁰. If such a reduction occurs, does this mean that the regulatory level under the TC rule will also be affected? If it is, additional waste streams may have to be handled as HW.

(3) As the regulatory pressures build, the need for more technical investigations regarding pollution prevention techniques will be required. The costs alone for managing HW streams and for characterizing these wastes will increasingly make the elimination of waste an economic necessity.

SUMMARY.

Implementation of the TC rule has had, and will continue to have, major impacts on how the Army manages its waste streams. Pollution prevention is the only viable alternative for long-term solutions to HW management. It is rapidly becoming an economic necessity to minimize all waste generation, not just HW. Increased emphasis will be required to insure that waste streams are scrupulously segregated and that good housekeeping practices are strictly enforced. In the short-term, use of existing EP TOX data, MSDS information, and other technical reports should be employed whenever possible to minimize the cost of chemical analysis.

REFERENCES

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3. EPA Manual, SW 846, Test Methods for Evaluating Solid Wastes, 3d ed, November 1990.
4. Memorandum, USAEHA, HSHB-ME-SH, 23 August 1990, subject: Hazardous Waste Study No. 37-26-0432-90, An Evaluation of the Impact of the Toxicity Characteristic Ruling on Army Waste Streams, June-July 1990.
5. USAEHA Technical Guide No. 146, October 1987, Pentachlorophenol-Treated Materials, Handling and Disposal.
6. Memorandum, Defense Industrial Supply Center, DISC-ET, 4 June 1990, subject: Test Results.
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8. Fonecon between Dr. C. Barkan, American Association of Railroads, and Mr. M. Brown, USAEHA, 25 July 1990, subject: Creosote-treated Wood.
9. Memorandum, CECOM, AMSEL-SF-REE, 5 June 1990, subject: Toxic Characteristic (TC) Study of Selected Military Batteries under Federal and State Hazardous Waste Criteria.
10. Advanced Notice of Proposed Rulemaking (ANPR), Comprehensive Review of Lead in the Environment under TSCA, 56 Federal Register 22096-22098, 13 May 1991.



Evaluation of the New Toxicity Characteristic Rule on Army Waste Streams

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HAZARDOUS WASTE IDENTIFICATION

LISTED:

- F-LIST: NON-SPECIFIC SOURCES
- K-LIST: SPECIFIC SOURCES
- P-LIST: OFF-SPEC. CHEMICALS/SPILL DEBRIS
- U-LIST: OFF-SPEC. CHEMICALS/SPILL DEBRIS

CHARACTERISTIC:

- IGNITABLE
- CORROSIVE
- REACTIVE
- TOXIC

CONSTITUENTS (EP TOXICITY)

CONSTITUENT	WASTE ID NO.	REGULATORY LEVEL (mg/L)
<u>METALS</u>		
Arsenic	D004	5.0
Barium	D005	100.0
Cadmium	D006	1.0
Chromium	D007	5.0
Lead	D008	5.0
Mercury	D009	0.2
Selenium	D010	1.0
Silver	D011	5.0
<u>PESTICIDES/HERBICIDES</u>		
Endrin	D012	0.02
Lindane	D013	0.4
Methoxychlor	D014	10.0
Toxaphene	D015	0.5
2,4-D	D016	10.0
2,4,5-TP (Silvex)	D017	1.0

TOXICITY CHARACTERISTIC CONSTITUENTS

CONSTITUENT	WASTE ID	REGULATORY LEVEL (mg/L)
<u>METALS</u>		
Arsenic	D004	5.0
Barium	D005	100.0
Cadmium	D006	1.0
Chromium	D007	5.0
Lead	D008	5.0
Mercury	D009	0.2
Selenium	D010	1.0
Silver	D011	5.0

TOXICITY CHARACTERISTIC CONSTITUENTS

CONSTITUENT	WASTE ID	REGULATORY LEVEL (mg/L)
<u>VOLATILES</u>		
Benzene	D018	0.5
Carbon tetrachloride	D019	0.5
Chlorobenzene	D021	100.0
Chloroform	D022	6.0
1,2-Dichloroethane	D028	0.5
1,1-Dichloroethylene	D029	0.7
Methyl ethyl ketone	D035	200.0
Tetrachloroethylene	D039	0.7
Trichloroethylene	D040	0.5

TOXICITY CHARACTERISTIC CONSTITUENTS

CONSTITUENT	WASTE ID	REGULATORY LEVEL (mg/L)
<u>SEMIVOLATILES</u>		
Vinyl chloride	D043	0.2
o-Cresol *	D023	200.0
m-Cresol *	D024	200.0
p-Cresol *	D025	200.0
Cresol	D026	200.0
1,4-Dichlorobenzene	D027	7.5
2,4-Dinitrotoluene	D030	0.13
Hexachlorobenzene	D032	0.13
Hexachloro-1,3-butadiene	D033	0.5
Hexachloroethane	D034	3.0
Nitrobenzene	D036	2.0
Pentachlorophenol	D037	100.0
Pyridine	D038	5.0
2,4,5-Trichlorophenol	D041	400.0
2,4,6-Trichlorophenol	D042	2.0

TOXICITY CHARACTERISTIC CONSTITUENTS

CONSTITUENT	WASTE ID	REGULATORY LEVEL (mg/L)
<u>PESTICIDES/HERBICIDES</u>		
Endrin	D012	0.02
Lindane	D013	0.4
Methoxychlor	D014	10.0
Toxaphene	D015	0.5
2,4-D	D016	10.0
2,4,5-TP (Silvex)	D017	1.0
Chlordane	D020	0.03
Heptachlor (& its Epoxide)	D031	0.02

TOXICITY CHARACTERISTIC COMPARISON (EP vs TC)

EXTRACTION PROCEDURE (EP) TOXICITY

8 METALS

6 PESTICIDES/HERBICIDES

TOXICITY CHARACTERISTIC (TC)

8 METALS

8 PESTICIDES/HERBICIDES

9 VOLATILE ORGANIC COMPOUNDS

15 SEMI-VOLATILE ORGANIC COMPOUNDS



TC COMPLIANCE DEADLINES

- 25 MARCH 1990: PROMULGATION DATE
- 27 JUNE 1990: NEWLY REGULATED GENERATORS
(>1000 kg/mo) NOTIFY EPA.
- 25 SEPTEMBER 1990: LARGE QUANTITY GENERATORS
(>1000 kg/mo) COMPLY WITH TCLP.
- 31 OCTOBER 1990: NEWLY REGULATED SMALL QUANTITY
GENERATORS (100–1000 kg/mo) NOTIFY EPA.
- 25 MARCH 1991: SMALL QUANTITY GENERATORS
(100–1000 kg/mo) COMPLY WITH TCLP.
- 25 MARCH 1992: NEWLY REGULATED LAND DISPOSAL
UNITS SUBMIT PART B APPLICATION.

TC MAJOR IMPACTS

- NEWLY REGULATED WASTE STREAMS
- GREATER WASTE ANALYSIS COSTS.
- SURFACE IMPOUNDMENTS

TC MAJOR IMPACTS

WASTE STREAMS

- SMALL ARMS AMMUNITION
- USED OIL
- PCP TREATED WOOD
- CREOSOTE TREATED WOOD
- PAINT WASTE
- BATTERIES
- PCB WASTE

CALCULATED CONCENTRATIONS OF TC CONSTITUENTS IN SMALL ARMS AMMUNITION

<u>Type</u>	<u>2,4,-DNT</u>	<u>Lead/Barium</u>
<u>5.56 mm</u>		
B, M193	79 mg/100 gm	38/37 mg/100 gms
<u>7.62 mm</u>		
B, M59	794 mg/100 gm	26/25 mg/100 gm
B, M80	None	26/25 mg/100 gm
B, Special, M118	737 mg/100 gm	25/26 mg/100 gm
<u>.45 Caliber</u>		
B, HPT, M1	80 mg/100 gm	26/34 mg/100 gm

TOXICITY CHARACTERISTIC CONSTITUENTS

CONSTITUENT	WASTE ID	REGULATORY LEVEL (mg/L)
<u>SEMIVOLATILES</u>		
Vinyl chloride	D043	0.2
o-Cresol *	D023	200.0
m-Cresol *	D024	200.0
p-Cresol *	D025	200.0
Cresol	D026	200.0
1,4-Dichlorobenzene	D027	7.5
2,4-Dinitrotoluene	D030	<u>0.13</u>
Hexachlorobenzene	D032	0.13
Hexachloro-1,3-butadiene	D033	0.5
Hexachloroethane	D034	3.0
Nitrobenzene	D036	2.0
Pentachlorophenol	D037	100.0
Pyridine	D038	5.0
2,4,5-Trichlorophenol	D041	400.0
2,4,6-Trichlorophenol	D042	2.0

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Hexachlorobenzene	D032	0.13
Hexachloro-1,3-butadiene	D033	0.5
Hexachloroethane	D034	3.0
Nitrobenzene	D036	2.0
<u>Pentachlorophenol</u>	<u>D037</u>	<u>100.0</u>
Pyridine	D038	5.0
2,4,5-Trichlorophenol	D041	400.0
2,4,6-Trichlorophenol	D042	2.0

TCLP MAJOR IMPACTS

SURFACE IMPOUNDMENTS

- REQUIRES SURFACE IMPOUNDMENTS/WASTEWATER TREATMENT SYSTEMS THAT TREAT TC WASTES MEET MINIMUM TECHNOLOGICAL REQUIREMENTS (MTRs).
- MTRs REQUIRE LINERS/LEACHATE COLLECTION SYSTEMS FOR SURFACE IMPOUNDMENTS.
- MTRs REQUIRE SECONDARY CONTAINMENT FOR TANKS.

TC MAJOR IMPACTS

WASTE ANALYSIS COSTS

- \$1500—\$2000/SAMPLE

ADDITIONAL INVESTIGATION NEEDS

- Direct Measure of Small Arms Ammunition Toxicity Characteristics.
- Alternative non-TC propellant mixtures.
- Alternative non-TC solvents.
- Lead painted contruction debris.

FUTURE IMPACTS

- Additional constituents.
- Lower Lead Regulatory Level.
- Increased Pollution Prevention.



RECOMMENDATIONS

- MINIMIZE ALL WASTE GENERATION (NOT JUST HAZARDOUS WASTE).
- SEGREGATE ALL WASTE STREAMS.
- USE MSDS/EP TOX DATA WHEREVER POSSIBLE TO MINIMIZE ANALYSIS COSTS.
- PRACTICE GOOD HOUSEKEEPING.

ASSISTANCE

WRITE:

COMMANDER
U.S. ARMY ENVIRONMENTAL HYGIENE AGENCY
ATTN: HSHB-ME--SH
APG, MD 21010-5422

CALL:

AV/DSN 584-3651/2953
COMM 301-671-3651/2953

TELEFAX:

AV/DSN 584-3656
COMM 301-671-3656



**Development of a Hazardous Materials/Hazardous Waste
Management Plan for the U.S. Army**

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ABSTRACT

The U.S. Army is a major user of hazardous materials and generator of hazardous wastes, having about 2.5 million metric tons treated and discharged, and 60,000 metric tons for disposal yearly. Some of these wastes are unique to the military, while others arise from common industrial production and maintenance activities. The Army has established goals concerning the generation and disposal of hazardous waste. Control and minimization of these wastes is complicated by the structure of the Army, which has established waste control as an "end-of-pipe" function and developed a network of agencies around that concept. In this structure, pollution prevention is difficult to attain, or quantify.

The Army needed a new structure and policies to reduce, manage and quantify its hazardous wastes and hazardous materials. A workgroup representing all the diverse Army activities developed a plan which included 13 issues, and made 57 specific recommendations for action. Actions were assigned to a lead, or principal, agency and to contributing agencies as appropriate. The plan was developed with the goal of establishing a framework to assess total life cycle costs including those from ultimate disposal and residuals from maintenance operations. Changes recommended represent new methods of conducting business in the Army. This paper describes the development of the plan and the actions recommended for implementation. Currently, the plan is under scrutiny to address several comments regarding suggested changes, primarily in the procurement process.

INTRODUCTION

The U.S. Army operates an industrial base of large magnitude, and its troop installations have all the aspects of small cities. Within its mission, the Army necessarily deals with a wide range of hazardous materials and generates a diverse mixture of hazardous wastes. Advances in technology have contributed to the magnitude and quality of materials used and wastes generated. However, the protocol with which the Army has managed its materials and wastes was established prior to the use of such advanced technology. This protocol included several "hand-offs" of systems, technology and

material which instituted disconnects in the life-cycle of weapons systems, vehicles, and support equipment. Such disconnects provide several impediments to the effective management of hazardous materials and hazardous wastes.

Impediments to pollution prevention include 1) development of new systems (e.g., vehicles, weapons) by activities which have no responsibility in the pollution control arena, 2) procurement policies geared to lowest initial cost, which do not require assessment of the maintenance or ultimate disposal costs, 3) a separate agency at the Department of Defense level which in the past had been responsible for all hazardous material and hazardous waste disposal without cost to individual Army installations and 4) a limited ability to track materials from procurement to disposal. These disconnects in management and impediments to pollution prevention were recognized at the highest levels within the Department of Defense, and resulted in DOD Directive 4210.15, Hazardous Materials Pollution Prevention.

A partnership between the principals involved was established to promote proper HM/HW management within the Army. This partnership consisted of the Assistant Chief of Engineers (ACE, responsible for overall coordination of HM/HW management for the Army), Assistant Secretary of the Army for Research, Development and Acquisition (ASA[RDA], responsible for systems development) and the Deputy Chief of Staff for Logistics ([DCSLOG], responsible for management of hazardous materials). The Five-Year Hazardous Materials/Hazardous Waste (HM/HW) Management Plan was developed as the blueprint of issues and actions to be addressed by the partnership. Development of the plan included evaluation of successful private industry waste reduction activities, analysis of Army doctrine in regulations, specifications and procedures, and assemblage of a workgroup representing various Army activities.

PRIVATE INDUSTRY EXAMPLES

Many companies have undertaken hazardous waste minimization (HAZMIN) and management programs in recent years. Major companies such as Union Carbide, Rohm and Haas, 3-M, and General Electric have corporate wide programs. Smaller companies with fewer resources may find it difficult to devote full time personnel to these programs, but they can often find support from state agencies. One such agency, the Illinois Hazardous Waste Research and Information Center (HWRIC), provides assistance to companies in developing new processes or evaluating existing processes. Information can be obtained on successful programs via a computer database.

Two companies which provided working examples for the Army were 3-M and the new GM Saturn plant. The 3-M company has a 3-P program, which stands for Pollution Prevention Pays. In this program, savings attributed to pollution prevention by process modification are tabulated and promoted. In the first year, 3-M estimated that the return on investment in HAZMIN was nearly one-half billion dollars. This program has strong central corporate support and is

highly publicized within the company.

The new GM Saturn plant has had a HM/HW management system since its inception. Materials are closely tracked throughout the entire plant, and life cycle costs (including environmental pollution control) of processes employed are assessed by a working group including both production personnel and environmental control personnel. The assessment includes both an analysis prior to purchase, and another to insure the safe use of the material. Two of the principal advantages of this arrangement is that neither production nor environmental control divisions of the company are dictating to others what processes are to be used, and the detailed tracking system (which functioned within a \$1.6 billion construction and startup project, with over 200 independent contractors) provided an excellent feed-back mechanism to chart progress toward meeting environmental goals.

The Army agency that acts as a central point of contact on HAZMIN, similar to that at HWRIC, in the Toxic and Hazardous Materials Agency (THAMA). In addition to technical and financial support, THAMA aids HQDA in a HAZMIN awards program. However, many Army programs are fragmented throughout Major Commands and Major Subordinate Commands and do not receive the strong central support necessary to succeed across the entire Army. Further, the Army is not able to track materials throughout its entire operation from logistics to disposal, and equipment developers (in the systems acquisition) usually dictate materials and procedures to end users without sufficient consideration of environmental consequences. Thus, these private sector examples provided an excellent database from which to identify shortcomings in the current Army program.

ARMY REGULATION ANALYSIS

During formulation of the Five-Year Plan, a related effort on Hazardous Waste Minimization Intervention within systems acquisition was underway. That effort took the form of three studies with the goal of identifying opportunities for hazardous waste reduction at various points during the life cycle of designing, developing and maintaining new and existing weapons systems. In Study 1, the acquisition process, Army regulations and technical manuals were reviewed to determine types of requirements for the enumeration and justification of hazardous materials in systems development.

These written instructions for acquisition are essential to implement Army policy and mission. Each establishes procedures for certain areas of authority or policy. However, many of the regulations have been written prior to the current level of concern for the environment. Thus, the instructions may give little or no merit to HAZMIN in laying rules for procurement. Within the Hazardous Waste Minimization Intervention study, 460 regulations were briefly reviewed, 120 were given a further, detailed review, and changes were suggested for 50 of the regulations, pamphlets, etc.

Although not directly a function of the development of the 5-year

plan, this review of acquisition regulations suggested the need for a much wider review of procedural instructions to eliminate or reduce barriers to proper hazardous material and hazardous waste management. In particular, military specifications (MILSPECS) and depot maintenance work requirements (DMWRs) place instructions on the handling of hazardous materials and generation of hazardous wastes in the use and maintenance of military hardware, ordnance. For older weapons systems, these can be 20 to 40 years old. Furthermore, items procured by performance specifications would provide no incentive for consideration of the potential for hazardous waste generation. Ultimately, the Army will need to review all use instructions to insure that environmental considerations are included.

FIVE-YEAR PLAN WORKGROUP

The most critical element in formulating the plan was the establishment of a workgroup representing the broad spectrum of Army agencies that would be affected by the plan. Table I lists the agencies and offices represented in the workgroup. This workgroup was patterned after the GM Saturn model, in which material assessment is performed by representatives from the complete organization, rather than by the environmental staff alone. From the same viewpoint, development of a plan to manage hazardous materials and hazardous wastes requires the input from all potential users and generators. Ultimately, tradeoffs will be required between production efficiency, retrofit costs and treatment costs.

Table I. Workgroup Participant Agencies

- Army Environmental Office
- Army Material Command
- Depot Systems Command
- Deputy Chief of Staff for Logistics
- Defense Logistics Agency
- Defense Reutilization and Marketing Service
- Engineer Housing Support Center
- Forces Command
- Office of the Assistant Secretary of the Army (Research, Development and Acquisition)
- Production Base Modernization Activity
- Training and Doctrine Command
- U.S. Army Construction Engineering Research Laboratory
- U.S. Army Environmental Hygiene Agency
- U.S. Army Logistics Evaluation Agency
- U.S. Army Toxic and Hazardous Materials Agency

The workgroup met formally twice in the formulation of the plan, and was asked to provide input and overall review within their agencies of several drafts of the plan. During the first meeting, the issues and constraints facing the Army pertaining to HM/HW were identified and categorized. The workgroup established a number of issues, in which one or more agency had specific experience. Several issues affected multiple agencies, resulting in a group

effort to describe the problem and propose solutions. As a result of the first meeting, assignments were made to various workgroup participants to draft the issue, and any suggested actions as discussed during the workgroup. Each issue had a lead, or responsible, agency and possibly other major contributing agencies. The draft issues were then compiled and redistributed to the workgroup for review.

Examples of the specific constraints presented, which were generalized as systemic issues, are as follows:

- 1) Funds are available to purchase equipment for implementation of HAZMIN techniques, but not for construction of any required buildings. Thus, one could purchase apparatus for paint removal by plastic media blasting, but could not construct the facility required to house it.
- 2) Materials purchased by performance specification must be compatible with the performance standards but not with any other materials currently in use. Thus, one provider of a material which meets performance specifications, and another provider also meeting specifications may result in providing materials which when mixed, become unusable and a hazardous waste, although each material individually met performance standards.
- 3) As the Army develops new weapons systems, there are many milestone reviews. However, none of these require consideration of adverse effects to the environment from the production, maintenance or ultimate disposal of the new system. Thus, all design and maintenance decisions are made without considering the complete cost of demilitarization and final disposal.

A second meeting of the workgroup was held to discuss the comments and consolidate them into an agreed form prior to issuing the plan as a final draft for comment throughout the Army. The result of the plan development was a series of 13 separate issues, with 57 actions assigned to 18 Army agencies. Most actions required multi-agency efforts, in which case one agency is designed as the lead responsibility, and others are designated as major contributing agencies. Table II shows the 13 issues identified through the development of the Five Year Plan, and Figure I shows the distribution of lead and contributing actions by agency.

Although the plan is divided into 13 Issues, three central themes emerged. They include Central Information/Coordination, Training and Education, and Authority.

Table II. Five-Year Plan Issues

- 1) Environmental Considerations in Systems Acquisition
- 2) Environmental Project Funding
- 3) Environmental Considerations in Procurement Policy
- 4) Technology Transfer and Implementation
- 5) Environmental Education and Training
- 6) Material Tracking and Quantification
- 7) Liability
- 8) Centralized Coordination of Effort, in partnership with ACE, DCSLOG and ASA(RDA)
- 9) Command Emphasis
- 10) Multi-Functional Effort
- 11) Environmental Staffing and Organization
- 12) Review and Update of Military Specifications and Procedures
- 13) Environmental Quality Control Committee, Charge and Authority

Central Information/Coordination

The Army is a diverse organization, and hazardous waste violations are often enforced state-by-state. This results in "islands of effort" wherein various agencies do not openly coordinate or share information. Issue 1) requires a source of technical information for methods to avoid hazardous waste generation by design changes during development. Issue 4) requires a "one-stop" centralized organization to transfer technology to the field and provide the incentive for change. Issue 8) needs one source to coordinate efforts, with the expertise to understand differences and minimize overlap of effort. At the installation level, Issues 3), 9) and 13) require a central body of expertise to provide input to purchase and use of hazardous materials, and to provide a high level, central POC for environmental problems.

Training and Education

Although a separate issue, it impacts several other issues as well, including Issues 6) and 8). The Army needs to elevate its consciousness to the environmental effects of its day-to-day operations. Implementation of the plan will require a new way of conducting business, and training will play a key role in its successfulness.

Authority

The environmental coordinator has not yet received a high level of authority on all Army installations. However, the requirements are ever increasing, as evidenced by some 30 new or revised laws passed in the last 20 years. Thus, although the environmental responsibilities and the requirements to interact with other activities (utilities, production facilities, etc.) have increased dramatically, no commensurate increase in authority has occurred. The plan seeks to increase authority not only by changing the position of the

ENVIRONMENTALLY ACCEPTABLE MATERIALS
TREATMENTS AND PROCESSES

MANTECH THRUST

PROGRAM REVIEW

20 JUNE 1991

CARMEN DIGIANDOMENICO

JACK W. HURD

ARMY ACQUISITION POLLUTION PREVENTION
SUPPORT OFFICE

BACKGROUND

THRUST AREA CRITERIA

- GLOBAL ISSUE
- WORLD CLASS EXECUTION
- MINI-FACTORY DEMONSTRATION

National Defense Center for Environmental Excellence

National Defense Center for Environmental Excellence
(NDDCEE)

SPONSOR: Deputy Assistant Secretary of Defense for the Environment

MISSION: To transition environmentally acceptable materials and processes to industry. To provide training supporting use of new environmentally acceptable technologies and to perform research and development where appropriate to accelerate transitioning new technologies.

STAFF:	o	Industrial Engineers	o	Materials Engineers
	o	Environmental Engineers	o	Industrial Hygienists
	o	Trainers	o	Scientists
	o	Support	o	Management

National Defense Center for Environmental Excellence

THRUST AREAS

- Export Environmentally Acceptable Materials and Processes to Industry
- Train All Levels of the Work Force On Proactive Approaches and Solutions
- Perform Research and Development Where Needed to Solve Problems

EAMTP PROGRAM SCOPE

- IDENTIFY COMPLIANT ALTERNATIVES
 - COATINGS
 - SURFACE PREP/TREATMENT/CLEANING
- VALIDATE PROCESSES/CONTROLS
- INCREASE WORKER SAFETY
- ESTABLISH MICRO-FACTORY
 - TECH TRANSFER TO FACTORY FLOOR
 - PROGRAM SHOWCASE - WORLD CLASS

Process Cost

Initial
Material
Cost

\$

Disposal Cost

Training, Reporting Record Keeping
Safety/Fire Precautions
Air/Water Pollution Control Residual Disposal

Big \$

MANTECH

ACCOMPLISHMENTS

- **NON-CHROME RINSE DEMONSTRATION AT
SCRANTON AMMUNITION PLANT**
- **PLATING ALTERNATIVE STUDY/TESTS**
- **COATING WORKSHOP**
- **ARMY LASER PAINT STRIPPING**
- **ION IMPLANTATION**
- **SOLVENT REPLACEMENT/DEGREASERS**

FY92 PLANS

CORE TEAM PROJECTS

**NON-CHROME RINSE - EXPORT TECHNOLOGY TO ALL OTHER USERS
PLATING ALTERNATIVE STUDIES - CADMIUM, CHROMIUM**

**COATING ALTERNATIVES - INSTALL POWDER COATING SYSTEM
AT CCAD**

- DEMONSTRATION OF E-COAT AT NDCEE

**PRETREATMENT ALTERNATIVES - CONVERSION COATING,
WASH PRIMER, ZINC PHOSPHATE**

ALPS - TASK IMPLEMENTATION OF TEST PLAN

FY92 PLANS

CORE TEAM PROJECTS (CONTINUED)

ION IMPLANTATION - OPERATIONAL EVALUATION

- DEMONSTRATION AT NDCCE

**SOLVENT REPLACEMENT/DEGREASERS - DEMONSTRATION TEST
AT LAAP**

**- DEMONSTRATION
AT CCAD**



FY92 PLANS

CONTINUING RELATED EFFORTS

- TRAINING PROGRAMS
- SERDP (ESTIMATED \$3 MILLION)
- DA AD HOC TEAM
- UNEP
- SBIR (ESTIMATED \$500,000)
- DoD TASK FORCE

SUMMARY

- ARMY ONLY SERVICE WITH DEDICATED MANTECH THRUST FOR POLLUTION PREVENTION
- DA VIEWS THRUST AS ARMY'S MODEL
- FY92 FUNDS ENSURE CONTINUATION OF TEAM EFFORT
- ADDITIONAL FUNDS CAN BE UTILIZED TO ACCELERATE TECHNOLOGY TRANSFER
- MANTECH FUNDS ARE COMPLEMENTARY TO OTHER FUND SOURCES (SERDP, NDCOE)
- SALARIES FOR POLLUTION PREVENTION SUPPORT MEET GEN. TUTTLE'S DIRECTION

Army Acquisition Pollution Prevention Support Office



OPTIMIZATION OF COMPOSTING FOR THE BIOREMEDIATION OF EXPLOSIVES-CONTAMINATED SOILS

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Roy F. Weston, Inc.

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The Army is focusing its technology development efforts on the remediation of Army-owned sites which have been contaminated from past operations. The production and handling of conventional munitions have resulted in the generation of approximately one million tons of explosives-contaminated soils at various military installations. The principle contaminants are trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylenetetranitramine (HMX). Depending on the concentrations present, these explosives-contaminated soils pose both a reactivity and toxicity hazard.

There are three types of operations which, in the past, resulted in explosives contaminated soils: the manufacture of TNT, the load assemble and pack of explosives into munitions, and the demilitarization of obsolete munitions. Each of these operations generated large amounts of water contaminated with explosives. In the past, it was considered acceptable practice to discharge this contaminated water into unlined washout lagoons. The Army is now actively pursuing means to prevent groundwater intrusion by cleaning up these sites. The current remediation option, high temperature incineration, is costly and essentially infeasible for small remediation sites due to the required, disproportionate capital expenditures for the incineration systems. Due to the large volume of soils contaminated with these wastes, incineration costs could exceed over \$1.5 billion.

Composting is currently being considered as a viable, cost-effective alternative treatment method for the remediation of explosives-contaminated soils. Results from bench studies, pilot scale tests, and field demonstrations have proven that composting is capable of biologically degrading explosives and reducing the toxicity to acceptable levels. The advancement of composting explosives contaminated soils to a full scale remedial technology has been hampered mostly by economics. Using the data from a field-scale static pile composting demonstration at



Louisiana Army Ammunition Plant, a full scale cost analysis study indicated that direct implementation of composting was more expensive than incineration for explosives-contaminated soils. Incineration costs are typically estimated to be between 300 to 600 dollars/ton for installations with less than 20,000 tons of explosives- contaminated soils and 200 to 300 dollars/ ton for installations with larger volumes. The unit cost for incineration varies with the amount of soil to be treated because of the requirements for excavation, mobilization and demobilization, incineration, and ash disposal. The cost analysis indicated that composting using static piles could compete with incineration economically if approximately a 28% soil fraction could be used in the mixture to be composted and the amendments kept below \$50 per ton. Since economics is the driving force in the implementation of new technologies, a composting optimization field demonstration was initiated.

An optimization field demonstration has been completed at a National Priority List (NPL) site to assess the operational aspects, economic aspects, and analytical aspects required for full scale remedial operations. Maximum soil throughput was evaluated using both aerated static piles and mechanically agitated, in-vessel composting systems. Although some of the data from the composting optimization study is unavailable at this time, the data from selected tests is presented. All three explosives, TNT, RDX, and HMX demonstrated significant reductions in all the tests performed, regardless of the initial concentrations. A direct comparison of aerated static piles versus mechanically agitated, in-vessel composting using a 10% contaminated soil loading with the same amendment composition mixture indicates that mixing significantly increases the degradation rate and therefore decreases the composting time. The majority of degradation in the static piles occurred in the first 44 days whereas, the majority of the degradation in three mechanical tests occurred within the first 10 days of the study. A comparison of two amendment compositions using 10% soil in the agitated composter was performed. Results indicated the type of amendment composition mixture selected can influence the reduction of RDX and HMX. One of the mechanically agitated composts exhibited superior degradation capabilities, and removed 99.8% of TNT, 99.3% of RDX and 94.9% of HMX. A final report on the compost optimization study will be available in September 1991 and it's associated report, "Toxicology and Chemical Characterization of Compost", will be available in December 1991.

Results from the composting optimization study are currently being used to develop a full-scale remediation design for Umatilla Depot Activity, Hermiston, Oregon. The amount of soil to be remediated is dependent on the depth of explosives contamination in the lagoons and the regulatory clean-up criteria to be met. Neither of these have been determined yet. The optimization study results indicate that with a composting design system that provides mixing, the composting of explosives-contaminated soils will be more economical than

incineration. A controlled windrow system is being considered for this site based on the amount of soil for treatment and the disproportionate capital costs associated with large mechanical in-vessel composters. Preliminary cost estimates have been determined however, they are subject to change based on the final results of the optimization study, lagoon contaminant characterization and toxicology study.

Composting offers a cost-effective innovative technology to remediate explosives contaminated soils. The Army is proposing the use of composting to remediate the explosive washout lagoons at Umatilla Depot Activity, Hermiston, Oregon. Environmental regulators are supportive of a full scale remediation using this technology and the decision to remediate the lagoons by composting is expected in 1991. If implemented, it will be the first application of composting to remediate hazardous wastes at an NPL site.



CHEMICAL AND TOXICOLOGICAL INVESTIGATION OF COMPOSTED EXPLOSIVES-CONTAMINATED LAGOON SOILS¹

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The effectiveness of composting to detoxify explosives-contaminated soil was evaluated using samples from a second field composting experiment conducted by Roy F. Weston, Inc. at the Umatilla Army Depot. Static composting piles containing 7, 10, 20, 30, and 40 volume % contaminated soil, 10 volume % uncontaminated soil (negative control), and 100% contaminated soil (positive control, not a compost) were sampled periodically during composting and were leached using the US EPA Synthetic Precipitation Leaching Procedure (SW-846 method 1312) and ultrasonically extracted in acetonitrile after the US Army CRREL method. Tests included Ames bacterial mutagenicity with tester strains TA-98 and TA-100 with and without S9 metabolic activation, toxicity to Ceriodaphnia dubia, oral toxicity screen with Sprague Dawley CD/CR rats, and determination of explosives and TNT metabolites by HPLC.

Composting resulted in considerable decontamination of the explosives-contaminated soil. The concentrations of TNT (the main explosive) in the aqueous leachates decreased rapidly with time of composting, and at the end of composting (day 90), were 23 - 74% those at day 0, with the greatest decreases observed for the lower volume % soil. Solubility of TNT (100 ppm in pure water at 25°C) appeared to be a limiting factor in its leachability in early stages of composting. The only metabolites detected in the leachates were 2-amino-4,6-dinitrotoluene (2-A-4,6-DNT) and 4-amino-2,6-dinitrotoluene (4-A-2,6-DNT). Analysis of the composts showed greater decreases in the TNT concentrations than did the leachates. At the end of composting, the final TNT concentrations in composts were 2 - 29% those at day 0. HMX decreased to a lesser extent, and RDX did not appear to be affected at all. In addition to the two monoamino metabolites, two diamino metabolites (2,4-DA-6-NT and 2,6-DA-4-NT) appeared in the composts near the end of composting.

Bacterial mutagenicity could not be detected in the leachates using the standard testing protocol, probably because of the large dilution from the 20:1 liquid:solid leaching ratio. However, testing acetonitrile extracts allowed examination of compost mutagenicity. The specific mutagenicity (TA-98 w/o S9) of the final composts was 1 to 48 % that of the day 0 composts, and 0 to 29 % that of the 100% contaminated soil. The 7 to 30 volume % piles exhibited better reduction of mutagenicity than did the 40 volume % pile. Mutagenicity was not detected in the negative control compost from uncontaminated soil, indicating that mutagenicity was associated with explosives or other products/byproducts from load and pack operation wastes. The mutagenic activity was mainly direct-acting (not requiring S9 metabolic activation), which is typical of explosives and other nitrocompounds.

The species determined by HPLC were able to account for ca. 5 to 24 % of the extractable compost mutagenicity (TA-98 w/o S9) at the start of the composting, with TNT contributing the bulk of the accounted mutagenicity. As the composting proceeded, the accountable mutagenicity decreased considerably, and only 3 to 15 % could be accounted by HPLC analysis at day 90, suggesting that the additional mutagens were not detected by the current analytical method.

The compost leachate toxicities to Ceriodaphnia dubia were very high at the start of composting, and some of the contaminated soil compost leachates from day 0 were more toxic than leachates of the 100

% contaminated soil. This suggests a toxicity contribution from the amendments, and indeed, even the leachates from the uncontaminated soil exhibited moderate toxicity at the start of composting. However, with time of composting, the leachate toxicities decreased and at day 90 of composting, leachate toxicities were ca. 5 to 40 % those at day 0.

In rat feeding experiments, no rat oral toxicity was detected in the three samples tested: 20 volume % contaminated soil compost at day 90, 100 % contaminated soil, and 10 volume % uncontaminated soil compost at day 90. This result is not surprising because ca. 10 g of 100 % contaminated soil would be needed to reach the LD_{50} calculated from the explosives concentrations in the soil and their published LD_{50} s.

The main conclusion from this study is that composting under the conditions at UMDA can effectively decrease the concentrations of TNT (and to a lesser extent, HMX but not RDX) to a few percent of their original values. Extractable bacterial mutagenicity and leachable toxicity to freshwater crustaceans are reduced by nearly an order of magnitude. The most efficient composting was with contaminated soil volumes of 20 % and less.

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PROCESS AND ECONOMIC FEASIBILITY
OF USING COMPOSTING TECHNOLOGY
TO TREAT WASTE NITROCELLULOSE FINES

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SUMMARY

An evaluation of the process and economic feasibility of using composting technology to dispose of waste nitrocellulose (NC) fines (slurried in water) from the Radford Army Ammunition Plant (RAAP) was undertaken by the Tennessee Valley Authority (TVA) for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA). Two general categories of composting technology were evaluated: (1) static pile processing in which the NC fines are mixed with composting amendments and stacked in long aerated piles, and (2) in-vessel processing in which NC composting is carried out inside a process vessel and the compost mix is handled by mechanical processing equipment.

For the static pile process evaluation, a detailed conceptual design was made to provide a basis for estimation of capital and operating costs. This design was then evaluated at two levels of waste NC fines throughput, 6000 pounds per day and 2000 pounds per day (dry basis).

For the in-vessel process evaluation, commercial and demonstration scale composting facilities were visited by TVA personnel to gather process and economic information. This information was then modified conceptually to reflect operation of the particular process with NC fines at a throughput of 6000 pounds per day. The in-vessel processes evaluated were:

Metcalf and Eddy (Paygro) process in Baltimore, Maryland
Fairfield process in Plattsburgh, New York
Ebara process in Seven Springs, Pennsylvania

The results determined that both types of composting technology, static pile and in-vessel, are technically feasible methods of disposing of waste NC in slurry form. However, recent studies of NC composting in a soil matrix indicate that the biological destruction rate of NC is slower than the destruction rate of commonly composted materials (e.g. sewage sludge). Based on these studies, it is expected that composting of RAAP's NC fines will require a longer-than-normal retention time and a relatively low initial concentration of NC in the compost mix.

The estimated cost of composting RAAP's NC fines is significantly lower than the estimated cost of incineration, an alternative method of destruction being considered by USATHAMA. According to a USATHAMA estimate, the cost of NC incineration is about \$2000 per dry ton of NC. In comparison, the cost of composting is estimated to range from \$455 per dry ton of NC (6000-lb/day process) to \$754 per dry ton (2000-lb/day process), based on the static pile process economic evaluation presented in this study.

Further laboratory and pilot-scale research work is recommended to determine optimum operating conditions and to establish an accurate design basis for a full-scale installation.



INTRODUCTION

The manufacture of nitrocellulose (NC) at Radford Army Ammunition Plant (RAAP) in Radford, Virginia, generates water streams containing waste NC fines. These fines settle and accumulate in various process lagoons and holding pits. In the past, fines which could not be recycled back to the process have been disposed by removing them from these collection points in the process and then burning openly.

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is working with RAAP to find a more environmentally acceptable method of disposing of waste NC fines. In 1987, USATHAMA contracted with A. D. Little, Inc., to study options for recovering and treating/disposal of Radford's waste NC. In their report A. D. Little, Inc., favored a three-step process involving cross-flow microfiltration for recovery, followed by alkaline hydrolysis and biological waste-water treatment for disposal. The success of the microfiltration tests conducted by A. D. Little, Inc., has prompted efforts to examine the possibility of using microfiltration to capture NC fines at key points in the process, where the NC is suitable for recycling to the process. However, it is still expected that even a fully successful recycling program would still leave a substantial quantity of waste NC fines.

Later, in a study conducted in 1989 by Roy F. Weston, Inc., for USATHAMA, it was determined that soils that have been contaminated with NC-based propellants can be successfully composted to destroy the NC contaminant. (This study was conducted using contaminated soils at Badger Army Ammunition Plant.)

USATHAMA has now contracted with the Tennessee Valley Authority (TVA) to examine the process and economic feasibility of using composting to destroy Radford's waste NC fines. This study seeks to determine from literature sources the approximate processing conditions that would be required to effectively compost NC and to propose conceptual designs from which capital and operating costs can be estimated.

The current state of technology in composting is such that composting processes can be divided into two basic categories: static pile and in-vessel. With static pile processes, any compostable organic material is mixed with recycled finished compost and other amendments (sawdust, straw, horse feed, etc.) and laid out in long piles called static piles. The piles remain in place until the organic material is fully decomposed and stabilized. Microorganisms in the piles are provided with oxygen by frequent mechanical turning of the piles and/or forced aeration, depending on the particular requirements of the organic material. (If the pile is mechanically turned to provide aeration, it may be referred to as a windrow rather than a static pile.)

The in-vessel composting processes are generally commercial or near-commercial processes in which composting takes place inside some type of vessel, and the compost materials are mixed, transported, and handled by mechanical equipment.



Both types of processes (static pile and in-vessel) are evaluated in this study. Due to the flexibility and simplicity of static pile processes, a detailed conceptual static pile design was made to provide a basis for the economic evaluation. The in-vessel processes were evaluated by gathering information from visits to working facilities and from literature sources. The information from each process was then modified in a theoretical way, as if the process were to be used to treat NC, to produce an economic evaluation of each process.

STATIC PILE PROCESS DESIGN AND ECONOMIC EVALUATION

Design Basis and Assumptions

The quantity of waste NC fines requiring compost treatment at RAAP is not currently well defined. USATHAMA, in conjunction with RAAP personnel, has been examining various process options for capturing and recycling waste nitrocellulose fines from internal streams in the NC production process. Depending on the option selected and the degree to which it is successfully applied, the quantity of NC fines that will ultimately require composting varies. If no waste fibers can be recycled and the NC production facility operates at full capacity, it is expected that the total quantity of NC (on a dry basis) requiring composting will be about 6000 pounds per day. Alternatively, a reasonably successful recycling program or production at less than full capacity is expected to leave about 2000 pounds per day of NC still requiring composting for disposal. For comparison of costs and land space requirements, both of these waste rates were evaluated in this study.

All of the information relating to the specific compost properties of NC was obtained from a USATHAMA report prepared by Roy F. Weston, Inc., (Weston) entitled "Field Demonstration-Composting of Propellant Contaminated Sediments at the Badger Army Ammunition Plant" (report CETHA-TE-CR-89061). This report details pilot-scale tests to compost NC in a soil matrix. Additional information of a general nature was also needed regarding good compost practices. This was obtained from open literature sources regarding the composting of more conventional substances such as sewage sludge. Information was also obtained from persons inside and outside TVA who are experts in the fields of composting and microbiology.

Although the Weston study is thorough in its presentation of NC composting in a soil matrix, additional information was still needed to produce a complete conceptual design. It is generally recognized that even after this feasibility study and economic evaluation is complete and accepted by USATHAMA, lab-scale and pilot-scale composting studies will be required to prove the basis for the full-scale facility at Radford. In the absence of this information, several assumptions were made using engineering judgment, indirect evidence, and theoretical considerations. These assumptions are as follows:

1. A primary assumption is that the Weston composting test results using NC in a soil matrix are also applicable to NC composting



outside of a soil matrix. None of the literature sources that were reviewed presented any information to refute this assumption.

2. The most critical and perhaps weakest assumption is that a 40-day compost retention time will be sufficient to reduce the NC to a concentration less than the targeted level of 50 mg/kg. This assumption is critical because the size of the composting facility is proportional to the retention time required. It is clear from the Weston data that most of the NC is destroyed within this time frame. In one Weston test, the concentration of NC was lowered from 5 percent by weight to 378 mg/kg in 42 days, a 99.2 percent loss (Table 4-7, page 4-18 of the Weston report).

Although this level is still above the 50 mg/kg target, two other assumptions must be taken into account. First, in a full-scale continuous operation, the microbial population in the compost will be highly acclimated toward NC as a food source due to repeated recycling. In the Weston study, the source of microbes was manure, and presumably these microbes would initially be acclimated to only those food sources in manure. Based on generally accepted principles of composting, it is likely that the presence of a microbe population fully acclimated to NC will be sufficient to overcome the small quantity of additional compost destruction that will be needed to achieve the 50 mg/kg target. Second, as the finished compost is loaded, hauled, unloaded, and spread during disposal, it will receive additional aeration and thus additional compost time to lower the NC content.

3. It is assumed that the initial concentration of NC in the compost should be about 5 percent by weight dry solids. This is less than the typical dry solids concentration range of 7 to 10 percent used in sewage sludge composting operations. Although the Weston report indicates that initial concentrations greater than 5 percent are compostable, the report also indicated that higher concentrations would require longer periods of composting. This would, thus, tend to offset the advantage of using higher concentrations. However, the main barrier against raising the concentration above 5 percent is the difficulty in achieving an acceptable carbon-to-nitrogen (C:N) ratio. This is discussed in detail in the next item.
4. It is assumed that the C:N ratio in the initial compost mixture can be as low as 10:1, instead of the more typical values found in sewage sludge composting which range from 15:1 to 30:1. This assumption is based on the fact that nitrogen in NC exists in an oxidized form, quite different from the reduced organic nitrogen forms that exist in most composted materials. Compounds containing reduced nitrogen, when composted at a low C:N ratio, tend to release large quantities of ammonia that retard microbial action and also produce an odor problem. Conversely, it is assumed that the oxidized nitrogen in NC will not convert to ammonia as quickly as the reduced forms, and thus a lower C:N ratio can be tolerated. Being able to operate at a low (10:1) C:N ratio is an important factor in holding down capital costs. If the C:N ratio is raised to 15:1, for example, system constraints will force the percentage



of NC to fall to about 4 percent in the initial compost mix, or else the proportion of recycle material in the mix will have to be lowered. However, the recycle proportion used in this design is already much lower than is normal for composting (27 percent versus a typical range of 50-60 percent). If the percentage of NC in the initial mix must be lowered to accommodate a higher C:N ratio, the facility size and the capital cost will rise accordingly. Therefore, the C:N ratio limitation is a key factor that must be known to produce a final composting design, and thus C:N ratio should receive significant attention in future lab-scale and pilot testing.

It is believed that a lower-than-normal recycle proportion can be tolerated with NC composting because of a relatively higher usage of fresh amendments (sawdust, wheat straw, etc.). These materials should provide the bulk porosity and moisture absorption that the recycle normally provides. However, with NC composting, as opposed to sewage sludge composting, the recycle material is a critical source of microorganisms for the next static pile in the compost cycle. Therefore, the low proportion of recycle material used in this design (27 percent) remains a concern. Actual testing will be required to determine the minimum recycle proportion needed to perform this function.

One final assumption must be made regarding the C:N ratio. It is assumed that about 67 percent of the carbon in the wood sawdust will be available to the microbes. Essentially, this includes all cellulosic forms of carbon, leaving only lignin behind. Wood cellulose is slow to release carbon, but the lengthy (40-day) composting time proposed for this design should make all of it available. If necessary, wood carbon may be made more readily available by composting at a temperature a little lower than 55°C.

5. It is assumed that the concentration of NC in the waste stream will be 10 percent by weight. This concentration is roughly equivalent to the concentration obtained when settled fibers in holding lagoons are slurried and pumped out. This is one method of recovery that has a good probability of being used according to RAAP personnel. However, there are many possible ways in which a NC fines waste stream could be generated, depending on the type of NC recycling and recovery process (if any) that is chosen to be installed. At present, there is a very wide range of possible concentrations, ranging from a low of 143 parts per million (poacher settling pits overflow) to a high of 25 percent (based on a stream concentrated by microfiltration).
6. It is assumed that destruction of pathogens will not be required for NC composting. A pathogen destruction cycle is generally required during sewage sludge composting because of the presence of disease-causing bacteria in sewage. Usually, this means that the compost mix undergoes restricted aeration for several days, allowing the compost temperature to rise to 70°C or more for sterilization. In terms of process equipment, pathogen destruction time adds to the size of the facility as either additional static pile length or as a special set-aside area for the pathogen cycle.

Since NC fines contain no pathogenic bacteria, no pathogen cycles should be required; although this may have to be proved to the appropriate regulatory agency. Since the NC facility will be started up using sewage sludge or horse manure in the initial mix, a pathogen destruction cycle may be needed at that time.

7. It is assumed that no curing cycle will be required for NC composting. Generally, after aeration and pathogen destruction, compost is stacked in the open for several days to allow it to cure or stabilize. For NC composting, the long 40-day composting time should provide sufficient time for curing.

Process Description

Two static pile designs were created--one capable of composting 6000 pounds per day dry NC and the other capable of composting 2000 pounds per day dry NC. The two designs are similar, differing only in number of static piles and pieces of equipment but not in operating philosophy.

Because of the large land area required for composting, it is assumed that the compost facility will be located at a significant distance from the NC production area, which is located inside a congested plant area. According to RAAP personnel, the most likely site for the facility is a flat, open field just east of the Continuous Automated Single Base Line (CASBL). This site is roughly 1.4 miles in a straight line from the farthest portion of the NC production area (C-Line). Most of the other potential sites would be in the Horseshoe Area of RAAP north of the New River and would also be about the same distance away from the NC area as the field east of CASBL.

At this stage of the design, it was not determined which method of transport would be used to carry NC slurry to the composting area--pipeline transfer, truck hauling, etc. To include estimated transport costs in the design, pipeline transfer was arbitrarily chosen as the transport method. A 4-inch pipeline having an estimated length of 2 miles and a 100-gallon-per-minute booster pump are included in the design. It was estimated that about 1 mile of new pipe rack would also be needed.

Equipment Layout: The 6000 pound-per-day compost design contains a total of 20 static piles, each static pile 60 yards in length. Each static pile is supported by a separate diked concrete pad and has a panel roof to keep rainfall or snow off the pile. A panel roof design was selected to provide access along all sides of the static pile for moving equipment and personnel and to provide air flow to disperse odors. The diked pad is considered necessary to prevent NC-contaminated leachate from escaping to the ground environment.

The 20 static piles are divided among four identical operating units, each having 5 static piles. Each operating unit contains its own separate set of operating equipment which includes (1) a 20,000-gallon NC slurry holding tank and pump, (2) a 15,000-gallon leachate holding tank and pump, and (3) an 8,000-gallon in-ground leachate sump and pump. These figures, as well as other design details presented in this section, were



calculated to allow for normal, smooth operation of the facility and for upset conditions. For example, a full charge of NC slurry to a single static pile is about 14,800 gallons (assuming the NC slurry concentration equals the design value of 10 percent). However, a 20,000 gallon capacity was provided for each unit's NC slurry holding tank to accommodate unusual operating requirements such as the need to make a larger-than-normal transfer of slurry from the NC area, a slurry weaker than 10 percent solids, pipe line flushings, etc.

Figure 1 depicts a single static pile and shows how it is interconnected to its operating unit's equipment. Each operating unit has a separate motor control center which also houses the instrumentation.

Normal Operation: Each static pile is operated in 40-day batch cycles. A portion of compost from the previous composting cycle is retained as recycle material to provide microorganisms to the compost. The recycle material is spread out using a front-end loader or 3/4-yard garden tractor to the normal length (60 yards) and width (9 feet) of the static pile. Slurry of fresh NC fines is pumped from the NC slurry holding tank (V-1) to a spray header located above and along the length of the static pile. The header has spray nozzles spaced along its length to distribute the slurry evenly over the pile. The recycle material acts as a filter to capture the NC fines. Excess water drains through a support screen beneath the pile into a collection channel (aeration channel) where it flows by gravity to the leachate sump (V-3). The leachate is reused as will be discussed later.

After the NC slurry has been added to the pile, two compost amendments (sawdust and wheat straw) are added on top of the pile using a front-end loader or garden tractor. The sawdust adds bulk to provide voids in the pile to facilitate good aeration. It is also a source of slowly released carbon during the long compost retention time (40 days). The wheat straw provides a source of quickly available carbon to initiate composting. The proportions of materials in the piles are as follows:

- 50 percent NC slurry (equivalent to 5 percent dry NC in the compost)
- 27 percent recycle compost
- 15 percent sawdust
- 8 percent wheat straw

The wheat straw may be replaced with any readily compostable cellulosic material. RAAP's waste cotton linters or wood pulp may be acceptable replacements.

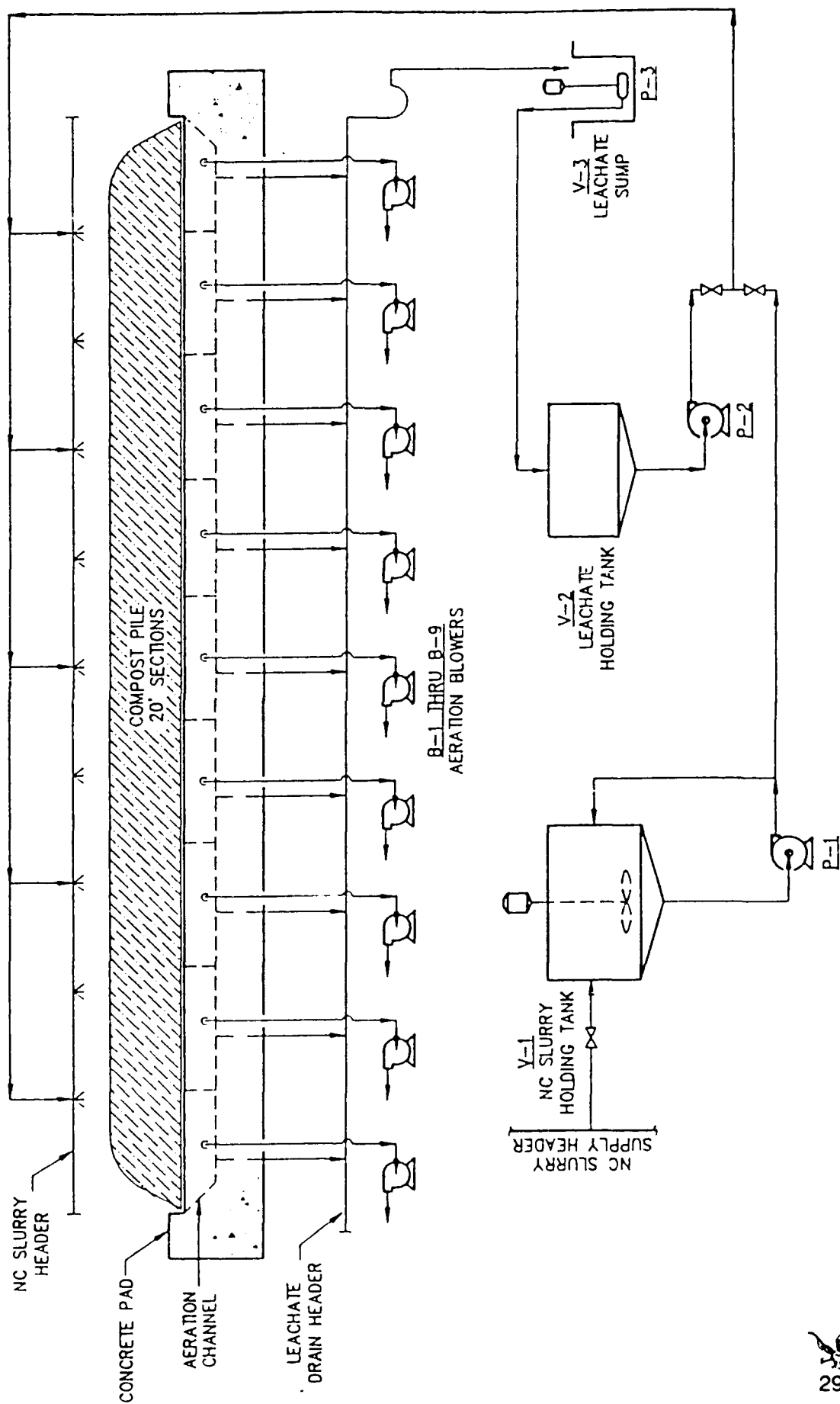
The pile materials are next blended in place to form a homogeneous mixture by using a compost turning machine. One such machine straddles over the static pile so that it may move along its length. Whirling blades below the cab of the machine mix and chop the compost materials as it moves. At this point, the pile is now prepared for its 40-day composting retention time.

Each static pile is aerated by nine vacuum air blowers (capacity 300 cfm each) located along its length. Each blower is dedicated to a separate 20-foot section of the static pile. Although there is no actual



Figure 1

COMPOSTING OF NC FINES STATIC PILE METHOD



division in the static pile, the aeration channel beneath the static pile is blanked off every 20 feet to direct the airflow through that section of the pile into the aeration channel and on to the vacuum blower. The static pile is sectioned off in this manner to maintain more even temperature control throughout the length of the static pile. Each 20-foot section has a separate temperature probe wired to a central controller housed in the motor control center. The controller maintains the temperature set point in each section by turning the blower on and off. (The normal set point temperature is expected to be 55°C to provide thermophilic compost conditions.) In addition to temperature control, aeration is also necessary to provide aerobic conditions for the microorganisms.

The aeration channel also serves as a drain point to capture leachate during NC slurry addition to the pile. The leachate flows by gravity to the leachate sump (V-3) from where it is pumped to the leachate holding tank (V-2).

Good composting conditions require that the moisture content of the pile be maintained in a range between 40 percent and 60 percent moisture.

The initial mix of compost materials, if applied all at once into a single mixture, would contain about 66 percent moisture, which is too high for good composting. However, since the NC slurry is applied only to the recycle material prior to adding the sawdust and wheat straw, it is expected that the recycle material will become saturated and allow a significant portion of the water in the slurry to pass through as leachate. The leachate can then be added back to the static pile over time by pumping out of the leachate holding tank into the same spray header used to apply the NC slurry.

Any NC fines that managed to pass through the recycle material bed would also be reapplied in this manner. It is likely that due to the lengthy composting time, additional water beyond what is collected as leachate will be required to maintain moisture conditions. Typically, with sewage sludge composting, the compost will dry from 60 percent moisture to 45 percent moisture in a 14-day period. Once the moisture content drops below 40 percent and stored leachate has been depleted, an outside source of water will be needed. Additional water can be made available at essentially no cost using the equipment arrangement in this design. For example, the 2-mile-long slurry transfer line will require periodic flushing to prevent settling and subsequent pluggage of the line. The flushing water could be supplied from the abundant excess of process water in the NC production area. This same process water could also be pumped directly to the composting area using the transfer line if more water were needed.

At the end of the compost cycle, about half of the finished compost (roughly 19 tons/day; equal to about 42 cubic yards/day) cannot be recycled and must be disposed of. Compost is a valuable soil amendment used in gardening and nursery operations. However, because of liability concerns, it cannot be sold or freely distributed to the public. Instead, it is suggested that compost be retained for landscape use or disposal on site at RAAP. There are a number of possible disposal options such as spreading it around shrubbery and trees in landscaped areas, spreading it onto grassy or wooded areas, filling in low-lying areas or ravines, or simply stacking it for later use. Sufficient equipment and labor are included in this estimate



to handle hauling, unloading, and coarse spreading. (Landscape or gardening use would require additional personnel and equipment which, it is assumed, would not need to be provided by the composting facility.)

Start-up: The waste NC stream does not contain the necessary ingredients to initiate and sustain composting, as do other commonly composted materials such as sewage sludge. In particular, the waste NC stream lacks a consortium (wide variety) of microorganisms and probably contains no microorganisms of any composting benefit. A consortium of microorganisms is needed so that there are at least a few species present having a greater natural tendency to break down NC. These species can then multiply and become more acclimated to performing their task. The engineers at Weston recognized this in planning their composting studies of NC-contaminated soil. They provided a microorganism-rich, nutrient-rich environment in their research compost piles with the amendments they selected.

The initial static piles at the RAAP compost facility should be composed of materials similar to those used in Weston's research. For the 6000-pound-per-day process, these materials include 508 tons of high-protein horse feed, 254 tons of sawdust, 1,414 tons of sewage sludge, and 300 tons of alfalfa. The compost retention time required to destroy the NC in this initial pile is expected to be longer than 40 days, perhaps exceeding 100 days as was experienced by Weston in tests using similar amendments to those listed above. After this initial charge, the next static pile in the cycle can begin normal operation, although the compost retention time may still exceed 40 days for a few cycles. The switch from startup operation to normal operation should take place quickly to force microorganisms to adapt to NC as a food source, thereby helping to quickly lower the compost retention time to its minimum.

Maximum and Minimum NC Slurry Concentration: To assist USATHAMA and Radford AAP personnel in selecting and costing process equipment which will be used to collect the waste NC fines, it is useful to determine the maximum and minimum NC concentrations acceptable for composting with the static pile design proposed in this report.

The maximum concentration that can be composted is unlimited, i.e., 100 percent, because water can always be added to the compost to achieve the proper moisture content for good composting. As a practical and economic matter, however, there is no need to concentrate the NC waste stream beyond a value that produces more than 40 percent solids (a good starting percentage) when added to the other compost amendments (recycle, sawdust, and wheat straw). This value is calculated to be about 14 percent NC by weight.

The minimum NC concentration in the waste stream can only be estimated. The minimum NC concentration must be based on the total quantity of water evaporated during the full 40-day compost retention time. If there is too much water in the waste stream, the quantity of recovered leachate from the piles will exceed the amount that can be added back to the pile and evaporated during the 40-day cycle. Excess leachate will then begin to accumulate in holding tanks, increasing in volume during each composting cycle. This excess must eventually be discharged. Presumably, the excess

leachate would contain NC fibers from the compost pile, and thus discharge would be environmentally unacceptable.

Rough calculations show that the NC slurry concentration in the waste stream should be no lower than about 4.5 percent for all of the excess water to be evaporated during a 40-day cycle.

Economic Evaluation

Capital and operating costs were estimated for both the 6000-pound-per-day process and the 2000-pound-per-day process. Based on each of the two process designs, the process equipment (including general piping arrangements) and the support facilities were specified in detail. Therefore, the accuracy of these estimates is in the region of plus or minus 20 percent. However, it must be reemphasized that even though the equipment is sized, the process design contains many assumptions that could greatly alter the costs after the process is fully developed. The potential cost impact of some of these design assumptions is discussed later.

For cost purposes, it was assumed that the compost facility would be a stand-alone facility. However, water and electrical hookups were assumed to be available within a distance of 1 mile and also some pipe rack (about 1 mile) was assumed to be available for use in the vicinity of the NC production facilities. Also, it was assumed that there would be no charge for the land.

For comparison, Table I lists all the major equipment pieces utilized in both size processes.

Capital Costs: Based on static pile process conceptual design and the major equipment list itemized in Table I, a capital cost estimate was prepared and is shown in Table II for both the 6000-lb/day process and the 2000-lb/day process. Total estimated costs were \$7.77 million and \$3.65 million, respectively. The estimates have been divided into six categories as follows:

1. Construction costs: The sum of all costs inherent in converting a design plan for material and equipment into a project ready for startup. This includes all construction labor (salary and benefits), process equipment (delivered to job site; includes items 1 through 11 in Table I), and other building materials (concrete, steel, lumber, piping, valves, instrumentation electrical supplies, etc.). Normally, part of this work would be done by a general contractor, but other specialized areas of work (such as the electrical installation, piping systems, and erection of buildings) would be done by subcontractors working for the general contractor.
2. Indirect and startup expense: The indirect and startup expense includes costs which do not become a final part of the installation but which are required for the orderly completion of the installation. These costs may include, but are not limited to, field administration, direct supervision, contractor's fees, insurance, and taxes. Startup costs are the costs that are incurred to bring the plant to full production. Startup costs may include employee training, process adjustments and/or capital expenditures

to correct a problem, report writing, and travel of consultants. The indirect and startup expense was estimated as 10 percent of the subcontract costs (which are part of the construction costs plus 2 percent of the total construction costs.

3. Profit and performance bond: For these estimates, the construction cost and indirect expense were added to the general contractor's profit calculated as 10 percent and the performance bond as 1.5 percent of that sum.
4. Engineering: Engineering includes the cost for the design and engineering, drafting, purchasing, accounting, reproduction, travel, and home office expense to produce documents and plans for the facility and to supervise the construction and startup process. Engineering cost was calculated by actual estimates of the work required for the job (number of drawings, man hours of engineering calculations, etc.).
5. Materials handling equipment: Materials handling equipment includes the cost for all compost turning and moving equipment. The number of pieces of equipment required for each of the two process sizes is shown in Table I (items 12 through 15). This equipment was capitalized, rather than expensed (i.e., rented or taken from RAAP's motor pool) because it will be utilized nearly 100 percent of the time by the composting operation. The cost of a single piece of each type of equipment is listed below.
 - a. Compost turning machine - self propelled
Written price quote: \$185,000
Vendor: Eagle Crusher Co., Inc., Galion, Ohio
 - b. Dump truck
16 cubic yard, tandem axles, diesel, 16-foot bed
Telephone Price Quote: \$51,363
Vendor: Anderson Ford, Florence, Alabama
 - c. Front-end loader
Caterpillar 936 E, 3 cu. yd. bucket, cab with air conditioner
Telephone price quote: \$110,170
Vendor: Thompson Tractor & Equipment Co., Decatur, Alabama
 - d. Scat-type front-end loader
3/4 cu. yd. wheeled/diesel
Estimating Manual: \$23,364
Englesman's Heavy Construction Cost File



TABLE I

Static Pile Process Major Equipment List

	<u>6000-lb/day</u> <u>process</u>	<u>2000-lb/day</u> <u>process</u>
1. Static piles, 60-yd concrete pad with roof	20	7
2. Fiberglass tanks, 20,000 gallon	4	3
3. Fiberglass tanks, 15,000 gallon	4	0
4. In-ground sumps, 8' deep x 7' x 7'	4	1
5. NC slurry pumps, 100 gpm @ 60' head	4	2
6. Leachate pumps, 50 gpm @ 30' head	4	1
7. Leachate sump pumps, 100 gpm @ 50' head	4	1
8. Blowers, 300 cfm	180	63
9. Booster pump, 120 gpm @ 260' head w/2 miles of 4" dia. transfer line	1	1
10. Mobile home trailer office	1	1
11. Motor control centers	4	1
12. Compost turning machines	2	1
13. Front-end loaders, standard	2	1
14. Dump truck, standard	1	1
15. SCAT-type loader, 3/4-cu. yd. scoop	1	1

TABLE II

Static Pile Process Capital Cost Summary

	<u>Capital Costs: (1990 \$)</u>	
<u>Category</u>	<u>6000 lb/day</u> <u>process</u>	<u>2000 lb/day</u> <u>process</u>
1. Construction costs (direct)	\$5,382,219	\$2,318,383
2. Indirect and startup expense	459,622	209,221
3. Profit and performance bond	679,206	293,098
4. Engineering	416,640	408,240
Total Fixed Plant Costs	<u>\$6,937,687</u>	<u>\$3,228,942</u>
5. Material-handling equipment	665,067	369,897
6. Initial charge of materials	<u>167,521</u>	<u>56,008</u>
Total Cost	<u>\$7,770,275</u>	<u>\$3,654,847</u>

6. Initial charge of materials: The initial charge of materials includes the cost of compostable materials to be used in startup of the static piles. Costs per ton were derived as shown below.
- Alfalfa, \$114.28/ton quote from Lauderdale and Colbert County, Alabama farmer's co-operative.
 - High-protein horse feed, \$240/ton quoted from same source as alfalfa above.
 - Sawdust, free to haul according to local sawmill operators, \$9.46/ton estimated hauling charge (assumed 50 miles one-way at \$1.00/mile using dump truck).
 - Sewage sludge, free to haul according to sewage plant operators, \$6.25/ton estimated hauling charge (same hauling assumption as for sawdust).

The total materials required for each size process are listed below.

	<u>6000-lb/day</u> <u>process</u>	<u>2000-lb/day</u> <u>process</u>
Alfalfa	508 tons	169 tons
Horse feed	254 tons	85 tons
Sawdust	1,414 tons	471 tons
Sewage sludge	300 tons	100 tons

For purposes of cost projection, it is useful to develop a mathematical equation relating the economy of scale to capital costs. By utilizing the cost figures from both facility sizes, an equation having a standard exponential format (often used to relate economy of scale) can be constructed as follows:

$$\text{Estimated capital cost, \$, million} = 7.77(R)^{0.68}$$

$$\text{where } R = \frac{\text{NC Flow Rate, lb/day}}{6000 \text{ lb/day}}$$

It should be noted that the exponential factor in the equation (0.68) is close to the factor widely used by the chemical industry to estimate overall plant economy of scale (0.6). This equation can also be used to approximately determine the impact that a change in design assumptions would have on the capital cost of a 6000-lb/day process. In this case, the value of R is substituted with a value equal to the relative impact of the design change on the size of the facility. For example, if experimental research shows that the compost retention time can be reduced from 40 days to 20 days, the number of static piles can be cut in half. Hence the new capital cost estimate can be determined:

$$\text{Capital cost} = 7.77 (20/40)^{0.68} = \$4.85 \text{ million}$$

Similarly, an increase in initial NC concentration in the compost from 5 percent up to 10 percent (without changing the compost retention time)

would also halve the facility size and would have the same impact on capital cost as the above example.

As a further example, this equation can be used to estimate the capital cost of a 6000 lb/day NC composting facility on the basis that it could be operated at conditions typically used for sewage sludge composting (14-day compost retention time and 8 percent initial concentration):

$$\text{Capital cost} = (7.77) [(14/40)(5/8)]^{0.68} = \$2.76 \text{ million}$$

Although this equation is only an approximation, it can be seen in the above calculation that the unusual operating conditions employed to compost NC have a large impact on the capital cost (\$7.77 million versus \$2.76 million).

Operating Costs: The operating costs for both facility sizes are shown in Table III. The total operating costs are estimated to be \$455 per ton of NC for the 6000-lb/day process and \$754 per ton of NC for the 2000-lb/day process. All operating costs are expressed on a dry ton of NC basis. Both cost estimates are significantly lower than USATHAMA's estimate for incineration (\$2000 per ton of NC). Incineration is an alternative destruction method being examined by USATHAMA. The \$2000-per-ton estimate is a rough estimate, because there are no data available regarding incineration of NC slurried in water.

In both cases, the largest expense category is labor, accounting for about 56 percent of the cost for the larger process and about 64 percent for the smaller. The operating crew shown on both tables is calculated on day shift only (40 hours per week); all manual activities are done during these hours. At night and on weekends, the only ongoing activity (temperature control of the static piles) can be maintained by the automatic instrumentation system.

The assignment of labor to a conceptual process can be rather difficult without the benefit of actual operating experience, so this is one cost category in which the estimate may have a fairly wide range of error. The remaining cost estimate categories have an accuracy of plus or minus 15 percent.

This equation should not be used to estimate the impact of proportional changes in the design assumptions (as was done with capital costs). A new equation was devised by analyzing the impact of design changes on each operating cost category:

$$\text{Operating cost, \$ per ton of NC} = 455 R^{0.36} \text{ (6000 lb/day size)}$$

where R = Proportional change in facility size brought about by changing the design assumptions.

In the previously used example where the compost retention time was theoretically reduced from 40 days to 20 days, the new operating cost can be estimated:

$$\text{Operating cost} = 455 (20/40)^{0.36} = \$355 \text{ per ton of NC}$$

TABLE III

Static Pile Process Operating Cost Summary

	<u>6000 lb/day process</u>		<u>2000 lb/day process</u>	
	<u>Annual</u>	<u>Cost Per Ton</u>	<u>Annual</u>	<u>Cost Per Ton</u>
	<u>Cost</u>	<u>of NC Fines</u>	<u>Cost</u>	<u>of NC Fines</u>
Personnel	\$278,500 ^a	\$254 ^a	\$176,300 ^a	\$483 ^a
1-Supervisor (1/4 time)				
4-Operators (6000 lb/day)				
2-Operators (2000 lb/day)				
1-Maintenance				
Compost Materials	89,600	82	29,868	82
-Wheat straw				
-Sawdust				
Utilities	85,200	78	44,134	121
Fuel, vehicle maintenance	25,400	23	15,200	42
Miscellaneous	<u>19,000</u>	<u>18</u>	<u>9,500</u>	<u>26</u>
Total	\$497,700	\$455	\$275,002	\$754

^a Includes 50 percent of salary in benefits plus 35 percent contractors overhead and profits.

It should be noted that there is potential for cost savings in the category of compost materials. Waste cotton linters or wood pulp from the NC production area may be suitable to substitute for wheat straw. (Any soft cellulosic material such as grass clippings or food waste may also be substituted). The quantity of wheat straw to be replaced every day is quite large, amounting to 4.8 tons per day. The potential savings are about \$53 per ton of NC fines.

As with capital costs, an economy of scale equation can be devised for the operating costs. However, when the operating costs are expressed on a per-ton-of-NC basis, the exponential scale factor becomes negative (i.e., operating costs on a per-ton-of-NC basis increase with decreasing facility capacity).

$$\text{Operating cost, \$ per ton of NC} = 455 R^{-0.46}$$

where R = Ratio: $\frac{\text{NC Flow Rate, lb/day}}{6000 \text{ lb/day}}$

Utilizing the preceding equation to estimate the theoretical operating cost for NC composting using the same operating basis as most sewage sludge facilities (14-day retention time and 8 percent initial concentration), the cost becomes:

$$\text{Operating cost} = 455 [(14/40)(5/8)]^{0.36} = \$263 \text{ per ton}$$

Land Requirements: By its nature, composting in static piles requires considerable land space. Land requirements are mentioned to aid in future planning and layout. The 6000-lb/day process is composed of four distinct units, each having five static piles plus dedicated equipment. Each unit covers an area with dimensions of approximately 80 yards by 100 yards. Each unit is independently operable, so the layout does not necessarily have to be contiguous. However, the units should be within a reasonable distance from each other to allow moving equipment (composters, front end loaders, etc.) to be shared by the units. In the case of the 2000-lb/day process, there is only one unit containing seven static piles. The overall dimension of the unit is about 80 yards by 140 yards.

IN-VESSEL PROCESS FEASIBILITY AND ECONOMIC EVALUATION

General Evaluation

A quite different approach was taken in the evaluation of in-vessel composting systems versus the approach used for the static pile system. In-vessel composting systems are generally automated package equipment designs developed by independent process developers. It is outside the scope of this study to reconstruct design details of these systems and modify them for NC composting. Furthermore, it was learned from visiting with system operators that the state-of-the-art in in-vessel system composting has not yet matured to full commercial viability. Operators are still experiencing difficulties and there are relatively few systems in commercial operation in the U.S. According to the December 1989 issue of BioCycle, out of 115 fully operational sludge composting facilities in the United States, only 21 are in-vessel type. However, far more in-vessel systems are in various stages of planning, design, or construction than static pile and windrow systems. This indicates that in-vessel systems are emerging as the preferred method of composting for the future.

The approach taken in this study was to evaluate specific in-vessel composting systems by answering three basic questions about each system:

1. Can this in-vessel system design be modified to compost 6000 lb/day or 2000 lb/day of NC fines in the form of a 10 percent slurry?
2. What is the approximate capital cost and operating cost of this in-vessel system after being modified for NC fines composting?
3. Does this in-vessel system have advantages or disadvantages compared with the static pile system design or compared to other in-vessel systems?

Of the in-vessel systems that were studied, generally all could be modified for NC composting. All of the systems can be resized to handle the long 40-day retention time for NC. The only system that may have a problem in this area is the Fairfield system. The Fairfield design utilizes a circular vessel in which the fresh compost begins at the outside of the circle and moves toward the discharge point in the center. Over a 14-day compost period, the compost pile shrinks as it loses water and carbon dioxide, closely matching the change in circumference as it moves inward. With a longer retention time the ratio between the outer diameter and inner diameter of the discharge port may have to be altered during design.

Two other areas of concern are (1) the use of large particle size wheat straw as an amendment (not commonly used in in-vessel sludge composting) and (2) excess moisture in the initial compost mix. Wheat straw can be ground or chopped separately and then added to the mix to achieve good particle size. If excess moisture is a problem, the NC slurry can be partially filtered (using any type of conventional filtration equipment) leaving a low volume of milky filtrate with a relatively low NC fines content. This filtrate can then be injected into the compost downstream at a point where compost has had sufficient time to partly dry. (In effect, the filtrate fills the same role that the leachate plays in the static pile system.)

In estimating the capital costs of the in-vessel processes, it was assumed that the added cost of equipping the process for NC composting would be completely offset by the deletion of sewage sludge handling equipment (storage bins, belt haulers, trucks, etc.).

Three in-vessel composting facilities were evaluated for this study. Two of these processes (the Metcalf & Eddy and the Ebara) were recommended by USATHAMA for study. The third (Fairfield) was selected by TVA on the basis that it has been widely discussed and analyzed in recent literature.

A fourth process (Royer, Royer Industries, Kingston, Pennsylvania) was scheduled for visit and evaluation but was subsequently dropped from consideration. Royer does not currently have a working prototype or a full-scale process, although a facility is scheduled to begin construction soon in South Carolina. However, since it appeared from Royer advertisements that their process was potentially less costly and more compact in size, TVA requested that they provide an informal capital and operating cost estimate based on process conditions provided by TVA. Initially Royer agreed, then later stated that the long retention time would make the compost reactor channel length too long to be practical. With the Royer design, the compost is gradually moved down long prefabricated channels.

One final point should be made before discussing the merits of the individual processes. The cost estimates for the three processes should be considered to be rough estimates at this stage of evaluation. It would seem improper to use these estimates for comparisons among the three individual processes. Rather, the estimates should be considered as three data points that can collectively represent a range of in-vessel processing costs.

Evaluation of Specific In-Vessel Systems

Metcalf and Eddy

Approximately 155 tons per day of sewage sludge from the city of Baltimore is composted at a facility operated by Metcalf and Eddy (M&E), an environmental services company. The facility sits on about 7 acres on the southeast side of Baltimore near the Chesapeake Bay. It employs 20 people and was built in 1985 at an original cost of 13 million dollars.

Process Description: The heart of the M&E facility (also known as a Paygro facility) consists of two long metal-wall channels that hold the compost mixture during aeration. Since each channel is operated batchwise, the operation is not continuous as are many other in-vessel processes. It resembles an in-vessel version of an aerated static pile operation. The channels sit side by side in an enclosed building.

Each batch begins by continuously mixing fresh sewage sludge with recycle compost and sawdust in a pug mill. The compost mixture travels on belts to an automated loading machine which fills a channel by traversing the width and length of the channel. The channel depth is about 10 feet. Aeration is provided by blowers that force air upward through the mix. The aeration rate is regulated to control the compost temperature at a constant 50°C. Periodically, the compost mixture is stirred using a machine called an Extractovator. The extractovator moves down the length of the channel, picking up small amounts of compost and then returning it to the pile. The retention time in the channel is normally 14 days.

The completed compost is removed by the extractovator and carried on belts outside the channel building to a holding area. Here, it undergoes restricted aeration to raise the temperature for pathogen destruction. After pathogen destruction, the compost is hauled by front end loader to a stacking area for curing. The finished compost is then sold to distributors outside the Baltimore area.

Capital Cost: A simple approach was taken to estimate the capital cost of a conceptual M&E facility modified for NC composting. First, the relative size of the NC facility, as compared to the Baltimore M&E facility, was calculated by ratio of the two compost reactor volumes. On this basis, composting 6000 lb/day of NC (at conditions of 40-day retention time and 5 percent initial mix concentration) would require a facility about equal to 69 percent of the size of the Baltimore facility.

Second, the inflation factor for construction costs must be taken into account. The Baltimore facility was built in 1985 at a cost of \$13 million. Using an economy of scale factor of 0.6, and escalating the cost into 1990 dollars using a construction cost index factor of 1.17, the following is obtained:

$$(\$13 \text{ million})(0.69)^{0.6} (1.17) = \$12.2 \text{ million (1990 cost)}$$

This cost is higher than the estimated capital cost of the 6000 lb/day static pile facility, which was estimated to cost \$7.77 million.

Operating Cost: The M&E personnel provided TVA with a complete breakdown of their operating costs. However, these costs cannot be directly adjusted and applied to a 6000-lb/day NC facility in the absence of specific information as to how the expenses were incurred. Therefore, some simplifying assumptions were made in adjusting these costs.

The Baltimore M&E facility directly employs 20 people, including operators, foremen, managerial staff, office personnel, and one full time analytical chemist. There are 8 operators out of these 20. For the 6000-lb/day NC facility, it was assumed that these eight people could reasonably be cut to four, due to the smaller size of the facility and the longer retention time (i.e., fewer loadings and unloadings of the reactors). As with the static pile estimate, it was assumed that the occasional need for managerial, clerical, and analytical support could come from sources already at RAAP without having to actually hire additional persons. Therefore, with four persons forming the core operating crew, it was assumed that the same crew that was proposed for the static pile facility could also handle a similar size M&E facility: one supervisor (1/4 time), four operators, and one maintenance.

The cost of compost materials (sawdust, wheat straw, etc.) was assumed to be the same as for the static pile facility because it is likely the same materials would be used. For the remaining cost categories of utilities, maintenance, technical services, and miscellaneous, it was assumed that these costs would be about 83 percent of the Baltimore M&E costs (assuming cost reduction will roughly follow a square root function, i.e., $0.69^{0.5} = 0.83$). Sludge transportation was assumed to be zero for the NC facility since long-distance trucking would not be required for NC.

Table IV shows a cost breakdown by category of the operating costs for the full-size Baltimore M&E facility and for the theoretical M&E facility composting 6000-lb/day of NC. The total operating cost for the theoretical M&E facility was about 70 percent higher than the static pile estimate (\$772 per ton of NC versus \$455 per ton).

One cost category that was much higher for the conceptual M&E facility was maintenance costs (\$182 versus \$23 for static pile). Higher maintenance costs could be expected for an automated compost-handling facility.

Discussion: TVA's overall impression of the Baltimore M&E facility is that it is a basically sound commercial operation. There are some mechanical problems that are relatively minor and are still in the process of being corrected. These problems mainly involve plugging at various points, generally bins and hoppers. If in the future USATHAMA selects a compost facility contractor, it is recommended that USATHAMA obtain a mechanical performance guarantee. (However, a process performance guarantee may not be easily obtained because NC is unusual as a compost material.)

There also appears to be a fairly severe corrosion problem on the building structural beams and other points except for the composting equipment itself. Apparently, this problem results from operation of the aeration blowers in an updraft mode, which pushes ammonia and moisture into



TABLE IV

Actual Operating Cost Summary for the Baltimore Metcalf
and Eddy Composting Facility Conceptual Costs
for a Facility Composting 6000-lb/Day NC

	<u>Annual Operating Cost</u>		<u>Cost per ton of NC fines</u>
	<u>Baltimore M&E facility</u>	<u>Theoretical M&E 6000 lb/day NC facility</u>	
Personnel	\$ 600,000 ^a	\$278,500 ^b	\$254
Compost Materials	120,000	89,600	82
Utilities	168,000	139,400	127
Maintenance	240,000	199,200	182
Technical Services	48,000	39,800	36
Sludge Transportation	180,000	0	0
Miscellaneous	<u>120,000</u>	<u>99,600</u>	<u>91</u>
Total	\$1,476,000	\$846,100	\$772

^a The personnel cost figure for the Baltimore M&E facility does not include benefits or contractors profit.

^b Includes 50 percent of salary in benefits plus 35 percent contractors overhead and profit.



the internal building atmosphere. In the winter, moisture condenses on the walls and ceilings. Originally, the aeration was designed to be operated in a down draft mode (i.e., vacuum), but the 10-foot deep compost beds tended to pack and restrict airflow. If the facility had been originally designed for updraft operation, I-beams and other metal parts could have been specified with the appropriate corrosion protection measures.

If land space becomes a limiting factor at RAAP, an M&E compost process would be ideal due to its compact channel geometry and its bed depth, which is twice that of typical static piles. M&E personnel stated that their site space of 7 acres was rather limiting for their operation, but this was due to the space needed to stack and hold the compost during curing. A curing cycle would not be required for NC composting due to the long composting time required.

Fairfield

Approximately 100 tons per day of sewage sludge from Clinton County, New York, and the city of Plattsburgh is composted in a facility designed by the Fairfield Engineering Company. The Fairfield facility, completed in 1986 at an approximate cost of \$7 million, was funded by a grant from the U.S. Environmental Protection Agency as an innovative technology demonstration project. Fairfield Engineering maintains an active role in the operation, maintenance, and ongoing modification of the facility, and has a full-time engineer on site.

At the time of TVA's site visit, the facility was down for repair and equipment cleanout.

Process Description: The Fairfield system utilizes two 116-foot-diameter circular-shaped digesters in which the compost mixture is aerated (14-day retention time). Operation is continual. A system of overhead mounted augers are used to periodically mix and move the compost from the outside of the circular bed to the discharge port at the center of the bed. As the compost bed moves inward, fresh compost mix is loaded along the outside circumference of the circular bed. Bed depth is approximately 9 to 10 feet. The circular geometry enables the bed to stay level as the compost mix moves inward and loses mass due to normal composting action.

Capital Cost: The Fairfield facility in Plattsburgh is very close to the size that would be required if the Fairfield equipment were employed to compost 6000 lb/day of NC. The capital cost was estimated by applying the construction cost index for 1986 (1.19) to the original cost of \$7 million. This gives an estimated cost in 1990 dollars of \$8.3 million. (Note that the cost index in 1986 (1.19) was actually higher than the cost index for 1985 (1.17) used in the M&E cost estimate. This was due to deflation in the construction industry during that time period.

Operating Cost: The Fairfield personnel provided TVA with a complete breakdown estimate of their operating costs. However, as with the M&E facility, these costs cannot be directly adjusted and applied to a 6000-lb/day NC facility in the absence of specific information as to how the expenses were incurred. Therefore, some simplifying assumptions were made.



The Fairfield facility employs a full-time operating crew of nine people plus a full-time representative from Fairfield. Using the same logic that was applied to the M&E facility, it was estimated that the number of operators could be reduced to four because of the longer retention time (fewer loadings and unloadings of the reactors). Therefore, the same crew (one-fourth supervisor, four operators, and one maintenance) that was proposed for the static pile facility was assumed to be able to handle a similar size Fairfield facility.

The cost of compost materials (sawdust and wheat straw) was assumed to be the same as the static pile facility because it is likely the same materials would be used. (It should be noted that Fairfield's wood chip cost of \$74,000 per month appeared to be very high, but since Fairfield's cost was not used to estimate this cost category, it has no impact on the NC facility cost estimate.)

Fairfield's utility cost was reduced for the NC facility estimate because of climatic difference between Plattsburgh, New York, and Radford, Virginia. Fairfield often has to preheat their air during the winter prior to compost aeration. This practice would not be required as often at Radford. Accordingly, the cost for fuel was reduced from \$24,000 per month to \$12,000 per month. The remaining utilities costs were assumed to be the same.

The last two cost categories, maintenance and miscellaneous, were assumed to be the same as currently experienced in Plattsburgh.

Table V shows a cost breakdown by category for the current Fairfield facility and for the theoretical Fairfield facility composting 6000 lb/day of NC in the same size equipment. As with the M&E facility, the operating cost was much higher than the static pile estimate (\$712 per ton of NC versus \$455 per ton). The operating cost of the theoretical Fairfield NC facility was comparable to the estimate for the theoretical M&E facility (\$712 per ton of NC versus \$772 per ton).

TABLE V

Actual Operating Cost Summary for the Plattsburgh Fairfield

Composting Facility and Conceptual Operating Costs

for Composting 6000 Lb/Day of NC

	<u>Annual Operating Cost</u>		<u>Cost per ton of NC Fines</u>
	<u>Plattsburgh Fairfield facility</u>	<u>Theoretical Fairfield 6000 lb/day NC facility</u>	
Personnel	\$ 480,000	\$278,500 ^a	\$254
Compost Materials	984,000	89,600	82
Utilities	334,000	190,200	174
Maintenance	192,000	192,000	175
Miscellaneous	30,000	30,000	27
Total	\$2,020,000	\$780,300	\$712

^a Includes 50 percent of salary in benefits plus 35 percent contractors overhead and profit.



Discussion: TVA's overall impression of the Fairfield facility is that it is still in the demonstration (or pilot) stage of technology development. Some of the problems they are experiencing are directly related to the extremely cold climate in Plattsburgh, which is near the Canadian border. However, many of the problems are systemic in nature. For example, the augers used to move compost through the circular digesters wear out at the tip and have to be replaced frequently. New auger designs are still being tested.

The Fairfield representative was particularly candid when discussing the problems that the facility was experiencing. Some problems, such as the auger problem, would likely have gone unnoticed if he had not volunteered the information. This must be taken into account when making relative comparisons of the in-vessel facilities. TVA's impression of the Fairfield facility is that many problems must be overcome before it can be considered commercial.

Like the M&E facility, the Fairfield facility offers an advantage of reduced land space requirements as compared with a static pile facility due to its use of large vessels to retain the compost mixture.

Ebara

Approximately 2 tons per day of food waste is composted in a demonstration-scale composting facility operated by Ebara Environmental Corp., the process developer. The facility is located in the mountains of southwest Pennsylvania near the Seven Springs Mountain Resort. The large restaurant facilities at the resort are the source of food waste for the process. The process is fully operational although some minor process modifications are still being made as might be expected for a demonstration unit. The facility was constructed in early 1990 at a cost of \$500,000. Ebara employs two engineers on site to oversee data collection, engineer process modifications, and troubleshoot process problems. One operator is employed.

Process Description: The Ebara compost reactor is an open-top channel made with concrete block walls to retain the compost mixture. Overall dimensions of the channel are approximately 7 feet wide by 45 feet long and 5 feet deep. The reactor is housed in a metal building.

The Ebara process uses a unique processing method in which the compost mixture is continually moved along the length of the reactor by a traversing paddle wheel. A typical compost cycle proceeds as follows: Food waste is hand loaded from plastic tubs into a short (2-3 feet) empty zone at the front end of the reactor channel. A small amount of recycle compost and fresh wood chip amendment are also loaded into the front end zone with the food waste. The food waste contains about the right combination of moisture, nutrients, and porosity to be compostable, so very little additional material is needed. The remainder of the reactor channel contains compost mix from previous operating cycles. The mixture at the rear end of the channel has been retained for 12 days and is fully composted. After the fresh materials are loaded, the operator initiates operation of the traversing paddle. The paddle first traverses the width of

the channel at the rear end, picking up and tossing the compost onto a moving belt. The belt carries the compost mix outside to the curing area. The paddle continues to traverse and move inward, mixing and tossing compost into the zone previously vacated by the tossing action. When the paddle reaches the front end, it leaves an empty zone where fresh material can be added. Air is pulled by a vacuum blower through the compost mixture to control temperature and provide oxygen for biological degradation. The vacuum blower pumps the air into an underground soil/gravel mix to remove ammoniacal odors. The finished compost is used in the many flower and shrub gardens at the resort.

Capital Cost: The Ebara demonstration facility is significantly smaller than the facility size that would be required to compost 6000 pounds per day of NC. Having a total volume of only 58 cubic yards, the Ebara unit is about 93 times smaller than the 5400-cubic-yard requirement for NC composting. Such a difference in size is likely to induce a large error when the capital costs are scaled upward to represent the full size facility. This should be taken into account when weighing the Ebara capital cost estimate with other in-vessel system estimates.

Since the Ebara demonstration facility was completed in 1990, no inflation factor was needed to make the capital cost estimate. Only the scale-up in size was used. Applying the standard scale-up factor of 0.6, capital cost is obtained:

$$\text{Capital cost, theoretical} = (\$500,000) (93)^{0.6} = \$7.6 \text{ million} \\ \text{for a 6000-lb/day NC Ebara facility}$$

This estimate is quite close to the estimated cost for the static pile system, \$7.77 million and is not far from the estimate for the Fairfield facility, \$8.3 million.

Because the scale-up factor for the Ebara facility was so large, TVA asked Ebara officials to make a rough theoretical estimate of the capital cost of a 5400-cubic-yard facility that utilizes Ebara equipment. Ebara responded with an estimate of \$4.5 million, which included the installed cost of the basic equipment: fermentation reactors with rotating paddle wheel, crane, aeration system, drainage system, temperature control system, soil odor filter, discharge conveyor, curing yard, and all necessary buildings. To this cost TVA added two front end loaders, a dump truck, utility hook-ups (service water, electrical), service road, and fencing. This brought the total capital cost estimate to a figure of \$5.8 million. It must be emphasized that this figure is based on rough calculations, not the cost of a working facility.

Operating Cost: The operating philosophy of the Ebara demonstration unit is typical of that found in pilot-plant operations. Thus Ebara's current operating costs would not translate to a commercial operation. When Ebara personnel made the above described capital cost estimate, they also roughly estimated some of the operating costs for a full-scale facility. Their estimate for labor included one manager and four operators. (No maintenance personnel were included.) Therefore, it seemed reasonable that the standard crew (one-fourth supervisor, four operators,



and one maintenance) proposed for all the other estimates could be used for the Ebara estimate. Ebara also provided figures for power (350,000 kWh) and maintenance costs (\$90,000). The remaining cost categories were predicted by using costs from the 6000-lb/day NC static pile estimate.

Table VI shows an operating cost breakdown for a conceptual Ebara facility composting 6000 lb/day of NC. The total estimated operating cost is \$471 per ton of dry NC. This is comparable to the estimated operating cost of the 6000-lb/day static pile process (\$455), but significantly lower than estimates for the two other in-vessel processes, Metcalf & Eddy (\$772) and Fairfield (\$712).

Discussion: The Ebara engineers arranged a demonstration run for the TVA investigative team during the site visit. The operation appeared to be mechanically sound. According to Ebara engineers, most of the equipment development is complete and the focus now is to fine-tune the process. Overall, the operation was impressive. Discussions with the Ebara engineers revealed that they were confident that the Ebara process could be adapted and scaled-up to compost 6000 lb/day of NC. A pilot facility similar in size to the Ebara facility would be appropriate to test NC composting to determine the potential commercial-scale viability of the process.

TABLE VI

Operating Cost Summary for a Conceptual Ebara

Facility Composting 6000 lb/day

	Annual Operating Cost	Cost Per Ton of NC Fines
Personnel	\$278,500 ^a	\$254
Compost materials	89,600	82
Utilities	23,350	21
Maintenance	90,000	82
Fuel, vehicle	15,750	14
Miscellaneous	19,000	18
Total	\$516,200	\$471

^a Includes 50 percent of salary in benefits plus 35 percent contractors overhead and profit.

CONCLUSIONS

- It is technically feasible to compost RAAP's waste NC fines using either a static pile composting operation that has been specifically designed to handle NC fines or a modified in-vessel facility.
- Based on research work conducted by Roy F. Weston, Inc., on composting of NC in soils and the current state of composting technology, it is assumed that (1) the time to compost NC down to a target concentration of 50 mg/kg (ppm) will be longer for NC (estimated 40 days) than for most compostable materials such as sewage sludge (14 days) and (2) the maximum initial concentration in the freshly mixed compost will be lower for NC (about 5 percent by weight) than for sewage sludge (about 8 percent by weight).
- The capital cost of a static pile composting facility that can process 6000 pounds per day of NC will be about \$7.77 million. For a smaller facility that can process 2000 pounds per day NC, the capital cost is estimated to be \$3.65 million.
- The operating cost to compost 6000 pounds per day of NC in a static pile facility is estimated to be \$455 per dry ton of NC. For a 2000-pound per-day facility, the operating cost is estimated to be \$754 per dry ton of NC. These costs are significantly lower than the estimated cost of incineration (\$2000 per dry ton of NC), based on USATHAMA's incineration estimate.
- The operating conditions required to compost NC have a major impact on the estimated capital and operating cost. If NC could be composted at conditions similar to those used for sewage sludge, then it is estimated that the capital cost of a 6000-lb/day NC facility could be reduced from \$7.77 million to about \$2.8 million and the operating cost could be reduced from \$455 to about \$263 per dry ton of NC.
- The capital cost of a 6000-lb/day NC in-vessel composting facility that utilizes commercially licensed technology will range from \$5.8 million to \$12.2 million. The operating cost will range from \$471 to \$772 per dry ton of NC.



RECOMMENDATIONS

- Laboratory and pilot-scale research should be performed on nitrocellulose composting. The research work should focus on finding ways to reduce the length of composting time and/or increase the initial concentration of NC in the compost mix. Listed below are some recommendations for future testing.
 - a. Determine the lowest carbon-to-nitrogen ratio that will not produce ammonia odor problems or retardation of the composting rate.
 - b. Examine the effect of pile temperature as a variable. Temperature should be studied at levels held constant throughout the composting time period and also studied by varying the temperature during the composting period.
 - c. Examine the effects of changing the relative proportions of amendment food sources (wheat straw, sawdust, etc.) in the compost mix. In particular, the possibility of reducing wheat straw usage should be examined. The cellulose in wheat straw is so readily available that the microorganisms may tend to use it exclusively instead of NC, if too much straw is present. However, at least some readily available cellulose is needed to encourage rapid growth of the microorganism population early in the compost cycle. A balance is needed to maximize the overall consumption rate of NC.
- An additional concern is that carbon sources in the pile may be consumed well before the end of the 40-day cycle, and the pile will run out of energy to maintain the operating temperature. Thus, the system may benefit from small additions of amendment food sources during the compost cycle. This should be tested.
- d. Perform routine testing of standard compost system variables, i.e. moisture content, pH, supplemental nutrients (phosphorus and nitrogen).
 - e. Examine the possibility of using anaerobic conditions (i.e., restricted aeration) during some portion of the compost cycle. Anaerobic conditions may be able to rapidly denitrify NC by reducing the oxidized nitrogen into ammonia, thereby leaving a cellulose molecule that is easily broken down. However, since ammonia may tend to retard microorganism activity during subsequent aerobic conditions, the anaerobic cycle must be tightly controlled to avoid excessive ammonia production.

- f. Determine the sequence of reactions which NC undergoes during biological breakdown by identifying the intermediate molecular species. At this time, the breakdown process of NC during composting is not well understood. (Current literature suggests the possibility that NC simply undergoes a partial loss of nitrate groups (denitration) instead of a complete breakdown to carbon dioxide, water, and nitrates). By obtaining a fundamental understanding of the NC composting process, the search for optimum composting conditions should be aided.
- A research study should be completed to determine the maximum concentration of NC that can be left in the finished compost and not cause an environmental problem when the compost is disposed. The concentration limit adopted for composted soils by Roy F. Weston, Inc., used by TVA for this study was 50 mg/kg, a limit that appears to be very stringent considering that NC's main hazard is its flammability. This work should be done in conjunction with the compost research work recommended above.
 - If in the future the Army chooses commercially licensed in-vessel technology to compost NC, mechanical performance guarantees should be obtained by contract from the licensor. At this time, in-vessel composting technology has not fully matured to commercial applicability, and it must be ensured that the contractor be responsible for onsite mechanical changes. Furthermore, if the licensor performs NC composting tests in their equipment for the Army and makes claims regarding the effectiveness of their process, a process performance guarantee should also be obtained.



AN ASSESSMENT OF THE APPLICATIONS POTENTIAL OF IN-SITU BIOTREATMENT FOR REMEDIATION OF SATURATED AQUIFERS

by

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ABSTRACT

For the past two years, the USAE Waterways Experiment Station (WES) has assessed the potential of in-situ biotreatment for remediation of contaminated aquifers. The objectives of this effort were to determine the knowledge gaps associated with in-situ biotreatment, identify knowledge gaps in applications methodology, and to develop a research program that will improve the field applicability of the technology. The assessment involved review of pertinent literature, discussions with key authorities in the field, interviews with individuals associated with companies having experience with the application of in-situ biotreatment at contaminated sites, and review of twenty-seven case studies.

A description of pertinent design components required for proper implementation is presented. The successes and failures of past attempts at implementing in-situ biotreatment are discussed.

INTRODUCTION

Biological destruction of organic contaminants has recently enjoyed much popularity as a potential treatment technology for remediation of contaminated sites. The increasing popularity of biotreatment is quite apparent while browsing through vendor displays at various national conferences, where not so many years ago, very few firms advertised expertise in biotreatment. However, at many recent conferences, there have been few firms advertising site remediation services that have not claimed to have expertise in biotreatment. Although, biotreatment is a



promising technology, it is not a panacea. Knowledge of the current positive and negative aspects of all configurations of biotreatment must be identified before the technology can be properly implemented at Army installations.

The USAE Waterways Experiment Station (WES) has been assessing the potential for implementing in-situ biotreatment at Army installations based on review of pertinent literature, interviews with key research and applications oriented personnel, and review of twenty-seven case studies. The objectives of this assessment were to evaluate the potential for implementation of in-situ biotreatment at Army installations, identify knowledge gaps that adversely affect the field implementation potential of in-situ biotreatment, and propose a research approach that can be used to develop in-situ biotreatment into a more "fieldable" technology. This paper briefly summarizes the findings of these efforts.

TECHNOLOGY DESCRIPTION

Biotreatment technologies can be divided into two main implementation categories; above-ground and in-situ. Use of above-ground systems requires excavation of the contaminated soils followed by treatment in above-ground reactors. Examples of such systems include land farming, composting, and bioslurry treatment. Contaminated soils can also be indirectly treated above-ground using pump-and-treat (PAT) systems. This is accomplished by removal of the contaminants from the soils via desorption into the groundwater followed by treatment of the groundwater in an above-ground bioreactor. The treated groundwater is injected back into the aquifer for recirculation through the contaminated portion of the aquifer. PAT systems are capable of treating both the contaminated soils and groundwater, but often require extended periods of time before cleanup standards are met (Travis and Doty 1990).

Whereas above-ground biotreatment systems use engineered, above-ground bioreactors, in-situ biotreatment uses the aquifer as the bioreactor. An engineered above-ground bioreactor can be designed and controlled to provide the required treatment conditions. Appropriately designed above-ground systems do not allow escape of contaminants into the environment, with treatment efficiencies easily determined. In-situ systems, on the other hand, use natural environments in which additives are strategically injected in an attempt to provide appropriate treatment conditions. Unlike a closed, engineered system, groundwater aquifers are not closed systems with complete access for determining the extent of treatment. It is difficult to determine the extent of contamination in an aquifer and even more difficult to completely control treatment conditions in them.



In-situ biotreatment is capable of treating both contaminated soils and groundwater. The concept of in-situ biotreatment is simple. Figure 1 illustrates a conceptualization of an implementation scheme for an in-situ biotreatment system. In this example, groundwater is removed from the contaminated aquifer using the dewatering well. Once above ground, the oxygen, nutrients, and surfactants (if desired) are added to the groundwater, which then is injected into the aquifer up-gradient from the site for transport into the biologically active zone (BAZ). Figure 1 illustrates only one of many configurations that may be used during the implementation of in-situ biotreatment. In some cases the groundwater is also treated above-ground using processes such as granular activated carbon, bioreactors, or air stripping (which could also be used as a means of aerating the water) to remove contaminants before enrichment with the additives and subsequent injection into the aquifer.

IMPLEMENTATION APPROACH TO IN-SITU BIOTREATMENT

The establishment of BAZs capable of degrading contaminants requires the presence of four essential environmental components: appropriate microbes, a carbon source(s), an electron acceptor, and inorganic nutrients. Each component is discussed separately below.

Microbes

Before any form of biotreatment can be initiated at a site, it is essential that appropriate microbial consortia capable of completely degrading the target contaminant(s) be present. Most contaminated soils already contain naturally-occurring microorganisms (indigenous populations) that have had the opportunity to adapt to the conditions and contaminants present at the site. Under these conditions, the components limiting the establishment of a BAZ are often not the presence of appropriate microbes nor food source(s), but rather the presence of an electron acceptor and/or suitable levels of certain essential nutrients or cosubstrates. However, at some sites where recent spills of xenobiotic compounds have occurred, the concentration of the contaminant may be so high as to be toxic. Alternatively, in soil where a new spill is first encountered by populations of native microorganisms, some period of time is required to permit the native organisms utilizing the spilled compound to reach population levels sufficient to remove significant amounts of the spilled compound. In the case where a microbial consortium is required to destroy the contaminant, time may be required for one or more key members of the consortium to reach population levels at which the consortium can function effectively as a unit. In other cases, a suitable degrading microorganism is simply not present. For example, Moris and Novak (1989) examined the



mineralization of tertiary butyl alcohol (TBA) using nitrate as an electron acceptor in two new contaminated soils. They concluded that one soil contained appropriate microorganisms (denitrifiers) to mineralize the TBA, while the other soil did not. They further concluded that understanding the ecological system is critical to the successful implementation of in-situ biotreatment.

Introduction of exotic microbes into a system is referred to as inoculation or bioaugmentation. This procedure has many advantages, if the added population is able to survive introduction into a foreign environment. However, a newly introduced microorganism faces many difficulties. The new organism must compete as an alien with native species already adapted to the environment for resources that are often scarce. The new organism must be able to contend with predators (often protozoans) and parasites (often viruses or other bacteria) present at the site. And the new organism must be able to adapt to the physical and chemical conditions present at the site. Nonetheless, addition of a new organism to a site may work, even for a short period, because the large numbers added temporarily overwhelm the opposing factors. Alternatively, if the new organism carries the genetic information for contaminant degradation in a transferable entity such as a plasmid, it may be possible for the degradation capability to be transferred to one or more native microorganisms which then have a better opportunity for survival and growth in the BAZ.

Since "appropriate" microorganisms are usually already present at the site, one must question why the contaminants persist. The reason that contaminants persist is that the soil ecosystem usually is deficient in one or more limiting components, preventing an increase in biological activity. Once the limiting component has been identified and added to the system, a BAZ capable of destroying the contaminant can be established.

Proper understanding of the microbial ecosystem present in the contaminated aquifer is very important in selecting the additives required to achieve efficient and effective biodegradation of the contaminants. In most cases, the basic microbiological conditions required for in-situ degradation of the contaminant(s) are fairly well understood. Recent advances in identification of specific microorganisms and key metabolic pathways involved in biodegradation of traditionally non-biodegradable compounds have spurred the recent increase in the popularity of biotreatment technologies. A good example is the application of methanotrophic microorganisms for degradation of trichloroethylene via an aerobic pathway (Wilson and Wilson 1989). Based on recent developments in microbiology, the basic microbiological considerations required for application of in-situ biotreatment are reasonably well-understood. The major

knowledge gaps that have been identified involve the applied aspects of microbiological concepts and the proper design of the delivery systems to maintain the environments required to establish BAZs.

Another area of microbiology critical to the success of in-situ biotreatment is an understanding of the biodegradation pathways required for complete mineralization of the contaminant. It is important that unacceptable degradation intermediates not be produced and accumulated in quantities that may pose more of a threat to the environment than the original parent compound(s). The biodegradation of trinitrotoluene (TNT) is a recent example of these concerns. Recent advances in the isolation of microorganisms potentially capable of mineralizing TNT have made in-situ biotreatment of TNT-contaminated soils appear feasible. However, there is a strong potential for the formation and accumulation of unacceptable intermediates and the extent of complete mineralization of TNT to carbon dioxide and water remains uncertain.

Carbon Sources

Organic food sources supporting the growth and activity of microorganisms are often referred to as carbon sources because the main elemental constituent of organic compounds is carbon. Supplying a carbon source to the microorganisms is often not a problem during in-situ biotreatment projects. Rather, the problem is the lack of microorganisms having the ability to degrade those food sources (contaminants) that are present. However, there are times when (a) the concentration of the contaminant is too low to support the growth of a degrading microorganism, or (b) initiation of contaminant degradation is too difficult for the contaminant to serve as an active carbon source. Under these conditions, it may be necessary to add food sources or cometabolites to the BAZ to support effective populations of degrading microorganisms. A good example of a cometabolite is methane required for the methanotrophic degradation of chlorinated solvents (Wilson and Wilson 1989). On the other hand, as suggested above, contaminants serving as carbon sources can also be present at elevated levels which can result in toxic or inhibitory effects. Some compounds may be biodegradable at one concentration and toxic at higher concentrations (Rozich and Gaudy 1985).

Electron Acceptors

Part of the process involved in microbial degradation of contaminants includes the transfer of electrons or energy to an electron acceptor. These electron acceptors are often one of the key components missing from a potential BAZ. Oxygen is the



electron acceptor supporting aerobic processes. Once oxygen has been depleted, many alternate electron acceptors are used by microorganisms to support anaerobic processes. These include: nitrate, manganese and iron complexes, and carbon dioxide. Using soil columns, Arthur et al. (1989) determined that oxygen was the limiting factor in establishing an active BAZ for their system. They further state that their conclusions substantiate the findings of others (API 1987).

The main problem associated with electron acceptors and the implementation of in-situ biotreatment is how to deliver the electron source into a BAZ at sufficient rates and concentrations. The delivery of electron acceptors presents several problems related to losses (sinks) during transport through porous media and poor hydraulic access into the potential BAZ. Raymond et al (1978) reported significant problems with the transport of both oxygen and nutrients into a contaminated aquifer.

Aerobic degradation of most contaminants generally supports the fastest degradation rates; however, oxygen transport through aquifers can be very difficult (Raymond et al 1978; Thompson and Ward 1989). The three main methods for introducing oxygen into an aquifer are diffusion of air/oxygen into the saturated zone using wells equipped with air diffusers; injection of air or oxygen enriched water into the aquifer; and injection of hydrogen peroxide into the aquifer (Raymond et al 1978; Thompson and Ward 1989).

Hydrogen peroxide is very reactive, and transport of this material through an aquifer can be very difficult (Thompson and Ward 1989). Natural soil constituents, such as iron, can serve as a Fenton's reagents, which catalyze the rapid abiotic degradation of hydrogen peroxide (Kuo 1990). In addition, hydrogen peroxide can also react with soil organic matter, resulting in the further loss of hydrogen peroxide (Thompson and Ward 1989). Consideration of hydrogen peroxide sinks and appropriate hydrogen peroxide concentrations [at higher concentrations (>2,000 mg/l) hydrogen peroxide is toxic to microorganisms] must be included in the design of an in-situ biotreatment system. Both factors will impact the design by affecting the configuration of the injection system and the design flow capacity of an additive feed system.

Although nitrate-supported anaerobic degradation is usually kinetically slower, nitrates seem to be more stable in aquifer systems than oxygen. Increased stability results in better transport properties in porous systems. Wilson et al. (1986) evaluated the use of nitrate as an electron acceptor to degrade organic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX). They concluded that these compounds could be successfully degraded under anaerobic conditions using nitrate as

the electron acceptor. Riss et al. (1988), using soil slurry systems operated in batch mode, were able to successfully obtain nitrate-supported degradation of fuel oils. There are some regulatory issues that must be worked out to use nitrate in groundwater aquifers. Nitrate is regulated in US Environmental Protection Agency's Drinking Water Standards. Proof that excessive amounts of nitrates are not escaping into the aquifer beyond the BAZ must be provided to ensure that the clean portions of the aquifer are not being contaminated with nitrates.

Nutrients

Nutrients are another key component that can affect the establishment of a BAZ. Nutrients are required by all living organisms for synthesis of new cells, with nitrogen and phosphorus being the two major nutrients most often limiting to microbial growth and activity. These nutrients are commonly referred to as macronutrients. Other inorganic compounds, referred to as micronutrients, are also required by microbes; however, the demand for these are low compared to that of the macronutrients. Most sites undergoing in-situ biotreatment only require the addition of the macronutrients because micronutrients are usually present in the soils in sufficient amounts.

Swindoll et al (1988) evaluated the effect of nitrogen and phosphorous on the biological degradation rate of various aromatic compounds in subsurface samples. They concluded that the addition of these nutrients generally induced microbial mineralization of the contaminants, indicating that the systems were nutrient limited.

As is the case for electron acceptors, the biggest problem identified with nutrients and in-situ biotreatment is the transport of the nutrients into the BAZ. It is essential that candidate nutrients not adsorb or react with constituents in the soil matrix, thus preventing their introduction to the BAZ. Van der Zee et al (1985) evaluated the fate of phosphate in non-calcareous soil and concluded that the reaction of phosphate with inorganic complexes can significantly reduce phosphate mobility.

Nutrients can precipitate in an aquifer, resulting in a reduction of the aquifer hydraulic conductivity (Thompson and Ward 1989). Reduction in the hydraulic conductivity of an aquifer undergoing bioremediation can be detrimental to the success of remediation activities. Groundwater flow through a contaminated area is one of the primary means, outside of excavation, that an aquifer can be remediated, whether biotically or abiotically. Therefore, extreme care must be taken to ensure that irreversible reductions in hydraulic conductivity do not occur.

OTHER FACTORS PERTINENT TO IMPLEMENTATION

Additive Delivery Systems

Delivery or application of additives required for establishing a BAZ is accomplished through the use of an additive delivery system. The two most commonly used procedures are well injection and trench infiltration systems. Selection of an appropriate system is very site-specific and dependent on such factors as site geohydrology, depth of the aquifer, permeability, and the required flowrate of the additives.

Microbial clogging of injection wells has been observed at PAT systems and municipal wastewater effluent recharge systems (Zappi et al 1990; Taylor et al 1990; Juboori et al 1974). Thompson and Ward (1989) suggest cycling the injection of additives then electron acceptors to prevent excessive microbial growth around injection systems. Injection of both nutrients and electron acceptors at the same time offers too rich an environment that can result in microbial fouling of the wells.

Hydrology

The hydrogeologic character of the aquifer is an important factor in the implementation of in-situ biotreatment. Remediation of aquifers with low hydraulic conductivity is difficult. By contrast, aquifers of high hydraulic conductivity are optimal for application of in-situ biotreatment, due to easy accessibility of the additives to the BAZ.

Modeling

Unlike above-ground bioreactors where treatment can be easily monitored, monitoring the progress of an in-situ biotreatment system can be difficult. A groundwater model is essentially the system operator's eyes into the system. Groundwater models should include algorithms that describe and/or predict transport of nutrients, electron acceptors, sorption effects, and contaminant decay rates. A proper modeling effort should be implemented prior to the construction of the delivery system in order to ensure optimal placement of the system components.

Surfactants

Surfactants or surface-active agents have recently received much attention for their ability to improve the solubilization



rate of hydrophobic organic compounds (Samdani and Shanley 1991). Surfactants are typically long chain molecules that are capable of reducing the interfacial surface tension between liquids or liquids and solids. Reduced interfacial tensions result in increased amounts of hydrophobic compounds going into solution, thereby increasing the accessibility of these compounds to microorganisms. Surfactants that are usually considered for application during bioremediation activities are commonly referred to as "green" surfactants. Typically, most green surfactants are anionic surfactants because they are the predominant surfactant type used in the preparation of products that may be ingested or contacted by humans. These surfactants are typically not toxic to microbes.

Changes in temperature, pH, or electrolyte concentration can each significantly alter the effectiveness of a surfactant (Samdani and Shanley 1991). Therefore, benefits of adding a surfactant for improving solubilization rate is matrix dependent and, therefore, site-specific.

The decision to use surfactants is usually based on the compound of interest's adsorption kinetics exhibited in the aquifer. Sorption kinetics have been found to have a significant effect on the observed biological degradation rate of the compound because degradation is dependent on the availability of the compound to the microorganism. Three hypotheses were identified concerning the ways in which contaminants, especially hydrophobic compounds, become available to microorganisms. The first and most widely accepted mechanism is that the microorganisms remain in the liquid phase while desorption kinetics release some of the sorbed compound into the liquid phase. This hypothesis basically assumes that the biodegradation rate is completely dependent on desorption rate. The second hypothesis is that some microorganisms are capable of producing surfactants that increase desorption rate through natural mechanisms. Consistent with the first hypothesis, once the contaminant has moved into the solution phase, the microorganisms proceed to degrade the contaminant. The third and final hypothesis is that some types of microorganisms are capable of degrading the contaminant while it is adsorbed onto the soil particle. Whichever hypothesis is correct, and all of them may be at one time or another, what is relevant is that microbial accessibility to the contaminant is critical. If a surfactant has potential to improve accessibility, it should be evaluated for potential application at a site.

Potential problems associated with adding surfactants during implementation of in-situ biotreatment are: 1) they exhibit a high oxygen demand in an ecosystem that is usually not oxygen rich, 2) sorption or chemical complexation of the surfactant onto the soil matrix which, in turn, hinders transport, 3) acceptance of a surfactant by state or federal regulatory agencies as a

candidate for injection into the subsurface, and 4) preferential degradation of the surfactant in place of the contaminant of interest.

REVIEW OF CASE STUDIES

A review of twenty-seven case studies of in-situ biotreatment was performed by the WES. The results of this review were used to determine the current state-of-the-art for implementation of in-situ biotreatment. The sources of information, as well as the quality of the information, were extremely diverse. Information on case studies performed by the private sector was limited. Unfortunately, this sector of the industry apparently has done the most work in terms of actual implementation of in-situ biotreatment. The private sector was very hesitant in releasing the negative aspects of the technology. By contrast, information obtained from government agencies and research facilities was very detailed.

Status of the Case Studies

Most of the case studies reviewed (66 percent) indicated that the remediation activities were considered complete. These case studies indicated reductions in overall contaminant levels; however, the percent removals of individual contaminants were rarely presented. The results from one site indicated that in-situ biotreatment was a failure at that site. Thirty percent of the case studies were still in-progress at the time our case study review was completed.

Aquifer Soil Characteristics

The majority of the sites contained aquifers composed of permeable soils such as sands, fractured limestone, and loam. None of the case studies indicated were conducted at aquifers containing soils having low permeability, such as clays. Problems associated with the hydraulic conductivity of the aquifer were not mentioned in any of the case studies. Intuitively, hydraulic conductivity can cause problems. For example, an aquifer containing contaminated clay lenses intermixed with sands can require a long time to remediate, because the low hydraulic conductivity of the lenses may prevent biological treatment of the contaminants from occurring in the lenses. Cleanup of the sands and not the clay lenses does not constitute success, because the lense can serve as a continual source of slow releases of contaminants into the sands over time.

Scale of Effort

The review indicated that forty-four percent of the case

studies involved full-scale remediation efforts that were smaller than five acres. Eleven percent of the sites were larger than five acres. Thirty-seven percent of the case studies did not indicate what scale of effort was expended. Finally, eight percent of the case studies were considered pilot-scale.

Implementation Scenarios

Half of the case studies used a combination of in-situ treatment coupled with an above-ground treatment system. This scenario removed the contaminants from the groundwater using an above-ground treatment system, added additives, then injected the additive enriched water back into the aquifer. Above-ground treatment systems used for treating the groundwater included air stripping, aerobic biotreatment, and activated carbon. The remaining half of the case studies used in-situ techniques alone for remediation of the sites.

Contaminants

Table 1 lists the various contaminant types and the percentage of the case studies containing these contaminants. From Table 1, sites contaminated with petroleum hydrocarbons were the most common, making up 70 percent of the case studies. This is consistent with discussions with research and applications personnel concerning the contaminants most commonly remediated using in-situ biotreatment. The remaining thirty percent were evenly split between solvents and other organics.

Microbiology

Table 2 lists the sources of microorganisms and percentages of the case studies using these sources for establishment of BAZs. The majority of the case studies (78 percent) claimed to have utilized indigenous microbes. Seven percent of the sites claimed to have used both indigenous and an exotic inoculum. Those case studies claiming to have used strictly non-endogenous microbes (15 percent), probably had some endogenous microbes that either assisted or actually completely degraded the target compounds. Survival or proliferation of the microbial seeds were not evaluated during any of the case studies.

None of the case studies indicated any problems associated with toxicity or inhibition of microbial activities due to contaminant concentration. Actually, none of the references indicated any problems associated with the microbiological aspects of the implementation efforts. It must be noted that the majority of the case studies involved remediation of sites contaminated with relatively well-documented, easily degraded



contaminants.

Electron Acceptors

Delivery of electron acceptors into potential BAZs was one of the biggest problems identified. Three methods of supplying electron acceptors to the BAZs were used in approximately equal percentages: injection of groundwater enriched using above-ground sparging (22 percent); sparging air or oxygen in a groundwater well (26 percent); or injecting hydrogen peroxide into the aquifer (30 percent). One site switched from using nitrate (anaerobic) to injecting hydrogen peroxide (aerobic) due to problems associated with transport of the nitrate through the aquifer. Approximately 11 percent switched from enriched water injection to hydrogen peroxide injection due to problems maintaining appropriate oxygen levels in the aquifer. These sites indicated an improvement in maintaining oxygen levels in the aquifer after switching to hydrogen peroxide.

Additive Delivery Systems

Approximately 80 percent of the sites used injection wells as a means of introducing additives into the aquifer for establishment of the BAZs. Another 15 percent used infiltration trenches. Two sites used a combination of both infiltration trenches and wells. One site treating a shallow saturated tank vault filled with pea gravel used a spray field for percolation of the additives into the BAZs. Approximately 20 percent did not state what type of delivery system was used. One problem identified at several sites was clogging of injection wells due to excessive microbial growth in the area immediately surrounding the well.

Summary

The following is presented as a summary of the case study review:

- a. Most attempts at in-situ biotreatment were at sites that were less than five acres in area and composed of relatively high permeable materials.
- b. The majority of the sites were contaminated with petroleum hydrocarbons.
- c. Injection wells were the most popular method of injecting additives, with microbial clogging of these systems being a potential problem.



d. All but one of the sites reviewed used aerobic biotreatment.

e. Approximately half of the case studies actually used a combination of both in-situ and above-ground treatment.

f. Delivery of required additives, such as oxygen and nutrients, posed significant challenges.

g. The majority of the sites utilized indigenous microbial populations instead of an exotic inoculum.

CONCLUSIONS

Based on our assessment, in-situ biotreatment has had some success during remediation of relatively small sites with good aquifer conditions (i.e. highly permeable soils).

While some basic microbiology research remains to be done, the major knowledge gaps are in the area of applications from both an engineering and microbiological standpoint.

In-situ biotreatment is not a panacea. The potential for implementation is very site specific with a standard protocol for evaluation potential not yet developed. Without the benefit of additional research and development, in-situ biotreatment should be confined to small sites with well defined aquifer systems.

ACKNOWLEDGEMENTS

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Table 1
Case Study Contaminant Types

Contaminant Type	Percent of Case Studies Containing This Type
Petroleum Hydrocarbons	70
Solvents	15
Other	15

Table 2
Microbial Sources

Microbial Source	Percent of Case Studies Utilizing this Source
Indigenous	18
Exotic Inocula	15
Both Indigenous and Exotic	7

Table 3
Electron Acceptor Sources

Electron Acceptor Source	Percent of Case Studies Utilizing this Source
Enriched water injection	22
Well Sparging	26
Hydrogen Peroxide Injection	30
Switched from Nitrate to Hydrogen Peroxide	4
Switched from enriched water injection to hydrogen peroxide injection	11
Not Stated	7

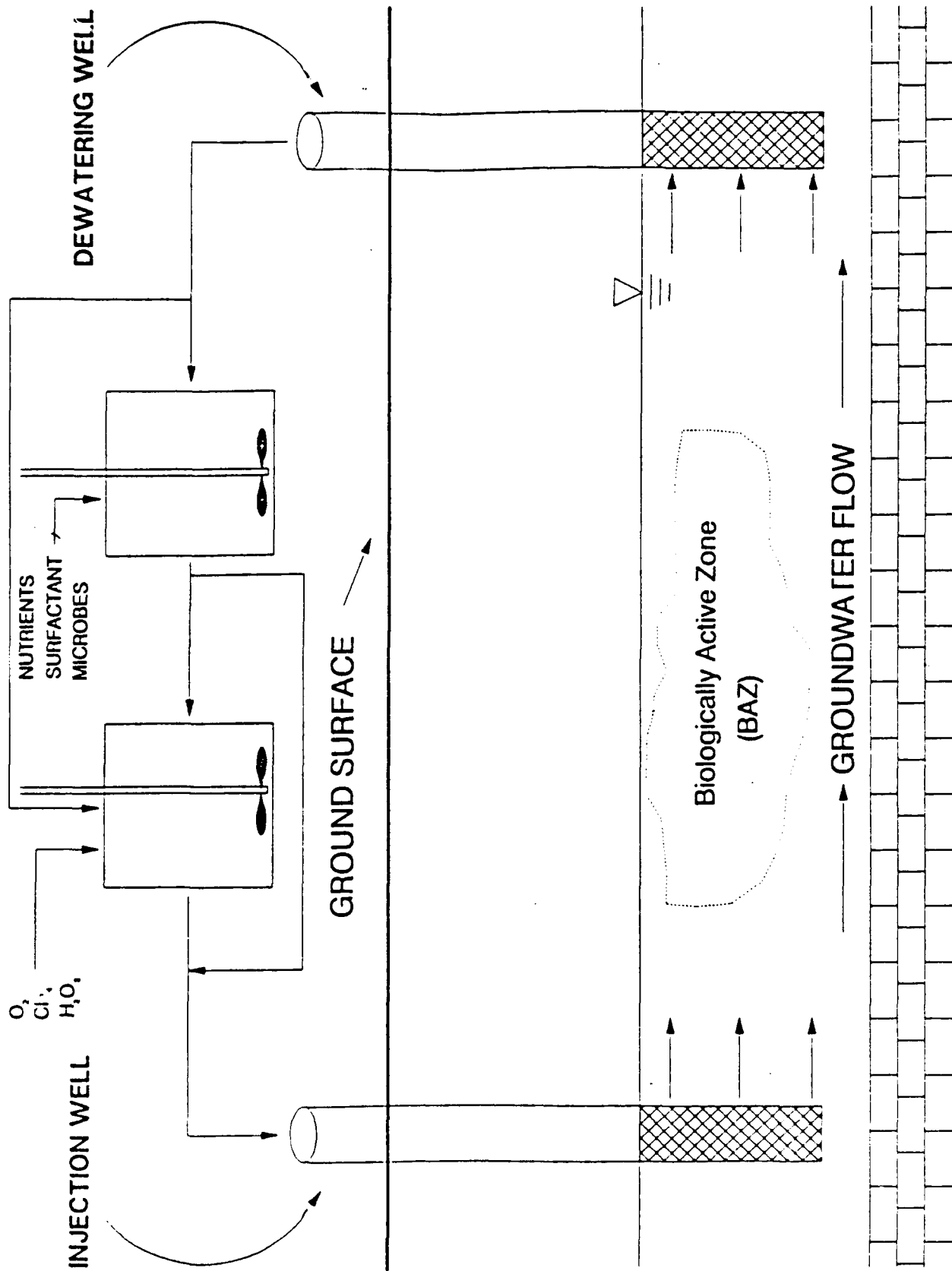


Figure 1.

CONCEPTUALIZED IN-SITU BIOTREATMENT SYSTEM



BIOLOGICAL TREATMENT OF BALL POWDER™ PROPELLANT PRODUCTION WASTEWATER

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INTRODUCTION AND BACKGROUND

Badger Army Ammunition Plant (BAAP), a GOCO facility operated by Olin Corporation, is one of two plants and the only military installation that manufactures BALL POWDER™ (BP) Propellant in the United States. Presently in caretaker status, mobilization plans require that BAAP be capable of treating its wastewater prior to discharge, in the event of activation. During the manufacturing process, wastewater containing ethyl acetate (EA), nitroglycerin (NG), dibutylphthalate (DBP), diphenylamine (DPA), and n-diphenylamine (nDPA) is produced. Table 1 summarizes typical expected BP wastewater concentrations. NG, DBP, DPA and nDPA are toxic and consequently limited to detection limits in the proposed Wisconsin Department of Natural Resources (WDNR) discharge permit (Table 2).

Previous work conducted at BAAP has indicated that NG can exhibit inhibitory effects on mixed biological cultures resulting in unacceptable system performance in terms of effluent BOD, TSS, NG, DPA, and nDPA concentrations. However, results from bench scale work [1] have indicated that NG can be effectively biodegraded via successive denitration steps through glycerol dinitrate and glycerol mononitrate isomers. The work presented herein explores the biodegradability of NG and its subsequent impact on traditional biological treatment processes. Removal mechanisms as well as the suitability of NG as a primary carbon source are also investigated.

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TABLE 1: BP PRODUCTION WASTEWATER COMPOSITION

COMPONENT	AVG. CONCENTRATION mg/L
BOD	910.
COD	1450.
ETHYL ACETATE	343.
NITROGLYCERIN	180.
DBP	1.2
DPA	2.0
2-nDPA	0.1
NO3 - N	27.
AMMONIA	10.
TKN	60.



TABLE 2: PROPOSED WDNR DISCHARGE LIMITS

PARAMETER	LIMIT
pH	6.0 - 9.0
BOD	30 mg/L Avg. ; 45 mg/L DAILY
NITRATE (NO ₃ - N)	50 mg/L
SULFATE	NO LIMIT ASSUMED
TOTAL PHTHALATES	DETECTION LIMITS (5 PPB)
TOTAL NITROSOAMINES	DETECTION LIMITS (5 PPB)
NITROGLYCERIN	DETECTION LIMITS (5 PPB)
TOTAL SUSPENDED SOLIDS	50 mg/L
TOTAL DISSOLVED SOLIDS	NO LIMIT ASSUMED
DISSOLVED OXYGEN	6.0 - 8.0 mg/L

EXPERIMENTAL PROTOCOL

A BP manufacturing pilot plant was operated to produce wastewater characteristic of that expected during full scale operation. The wastewater from this manufacturing process was subsequently treated in an oxic/anoxic sequencing batch reactor (SBR). The first two phases of the study required that BP be manufactured without the use of NG so that the biological culture could be slowly acclimated to both the background wastewater and NG. The final phase utilized BP wastewater as expected during full scale operation. Table 3 summarizes the study approach.

TABLE 3: STUDY APPROACH

Phase I	Acclimation to BP Wastewater without NG
Phase II	Acclimation to NG
Phase III	Representative Process Wastewater

Nitrogen and phosphorous were added in the form of ammonium chloride and phosphoric acid, respectively, to insure nutrient availability. A ratio of BOD:N:P of 100:7:2 was maintained to insure safe operation. Alkalinity in the form of NaHCO_3 was added to insure pH stability during nitrification. Based on the stoichiometric requirements of nitrification by *nitrosomonas* and *nitrobacter*, the influent was supplemented with ca. 8.5 g of HCO_3^- per gram of NH_4^+ added. Additionally, the stoichiometric alkalinity requirements for the biodegradation of NG were calculated based on varying cell yields (Figures 1 and 2). Given that the alkalinity requirements decrease with increasing cell yield a conservative yield value of 0.06 mg biomass/mg NG degraded was assumed. Consequently, approximately 650 mg/L of total NaHCO_3 as CaCO_3 was added to the influent. A F:M ratio of approximately 0.10 was maintained throughout the study. Mixed liquor volatile suspended solids (MLVSS) ranged from approximately 4,000 to 4,500 ppm. A minimum COD:NG ratio of 10:1 was maintained to insure carbon was the rate limiting nutrient. At higher NG concentrations EA was added to the influent to maintain this ratio. Dissolved oxygen (DO) concentration of approximately 4 ppm was maintained during the oxic phase. The DO concentration dropped to below 1 ppm after approximately 15 minutes into the anoxic phase. Energy input via mechanical mixing was provided to all cycles except fill and sedimentation. No mixing was conducted during fill cycles since it was observed early in the study

FIGURE 1: STOICHIOMETRIC DEGRADATION OF NG

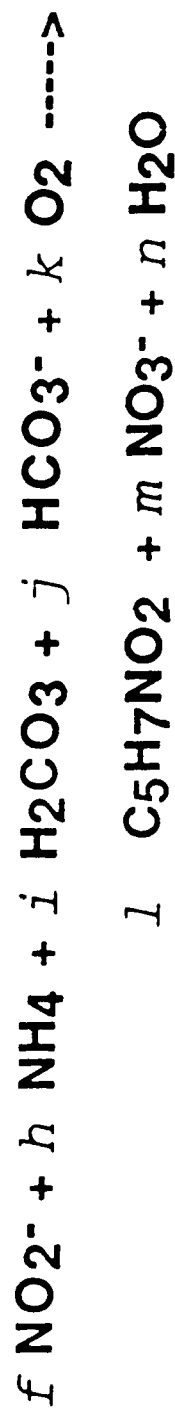
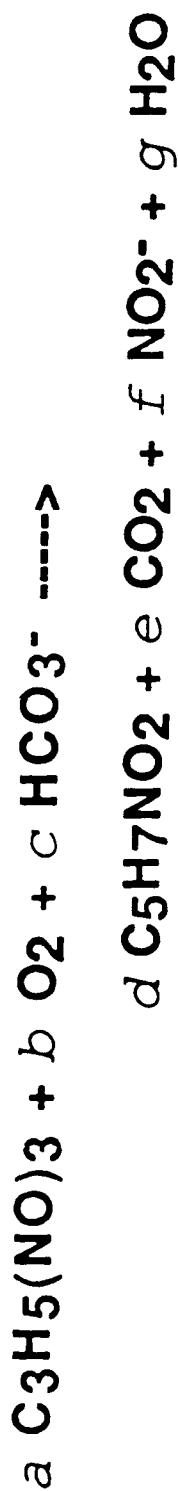
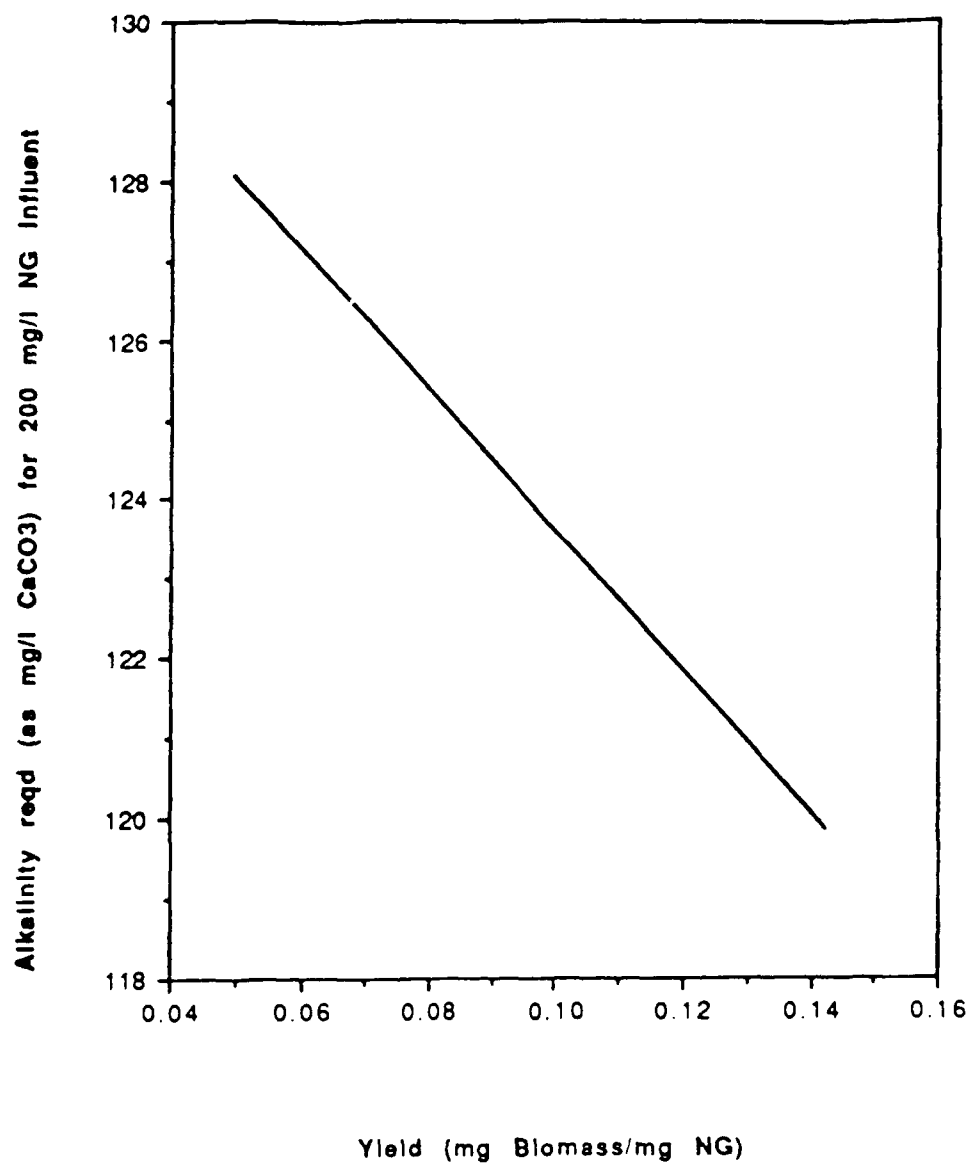


FIGURE 2: ALKALINITY REQUIREMENTS AS A FUNCTION OF CELL YIELD FOR BIODEGRADATION OF NG



that settling characteristics deteriorated significantly when mixing occurred in this cycle.

During Phase II NG was incrementally added to the influent up to the expected influent concentration of ca. 180 ppm. NG step increases ranged from 5 to 40 ppm. Approximately 5 days of acclimation per incremental NG concentration were allowed to insure process stability.

Once a NG-acclimated biomass was established, an aerobic bench-scale reactor utilizing the acclimated biomass was started. To investigate the potential for using NG as a sole carbon source, the feed consisted of a nutrient broth similar to that used during BOD assays and only NG as a carbon source.

The fate of NG in the reactor was ascertained by monitoring the aqueous phase and biomass concentrations of NG during a typical treatment cycle.

Traditional analyses (e.g. BOD, TSS, $\text{NO}_3\text{-N}$, etc.) were conducted in accordance with *Standard Methods*. NG, DBP, DPA and nDPA were assayed by a commercial laboratory using solvent extraction and reverse phase isocratic high performance liquid chromatography.

Two SBR cycle schemes (A and B) were utilized during this study (Figures 3 and 4). The only difference between the two is the length of the fill and idle cycles. Scheme A employed a 2.5 hour fill cycle and a 5.75 hour idle cycle. Scheme B employed a 4.0 hour fill cycle and a 4.25 hour idle cycle. Figure 5 illustrates that increased fill cycle and a decreased idle cycle times (scheme B) appears to improve system performance. Although the 24 hour total cycle time is twice as long as that utilized by the previous study, work [1] has indicated a long (84 hr) residence time may be required to degrade NG.

RESULTS AND DISCUSSION

Figure 6 illustrates the step increases in NG during the acclimation phase as well as the SBR effluent NG concentration. Figure 7 shows a concomitant increase in NO_3^- concentration in the influent at approximately the same time NG was added indicating that NG can impact NO_3^- assays. Based on the sharp decrease in effluent NO_3^- concentration, it also appears that a denitrifying population became established shortly thereafter (~day 90). Figures 8 - 10 indicate that no influent NG concentrations

FIGURE 3: SBR CYCLE TIMES: SCHEME A

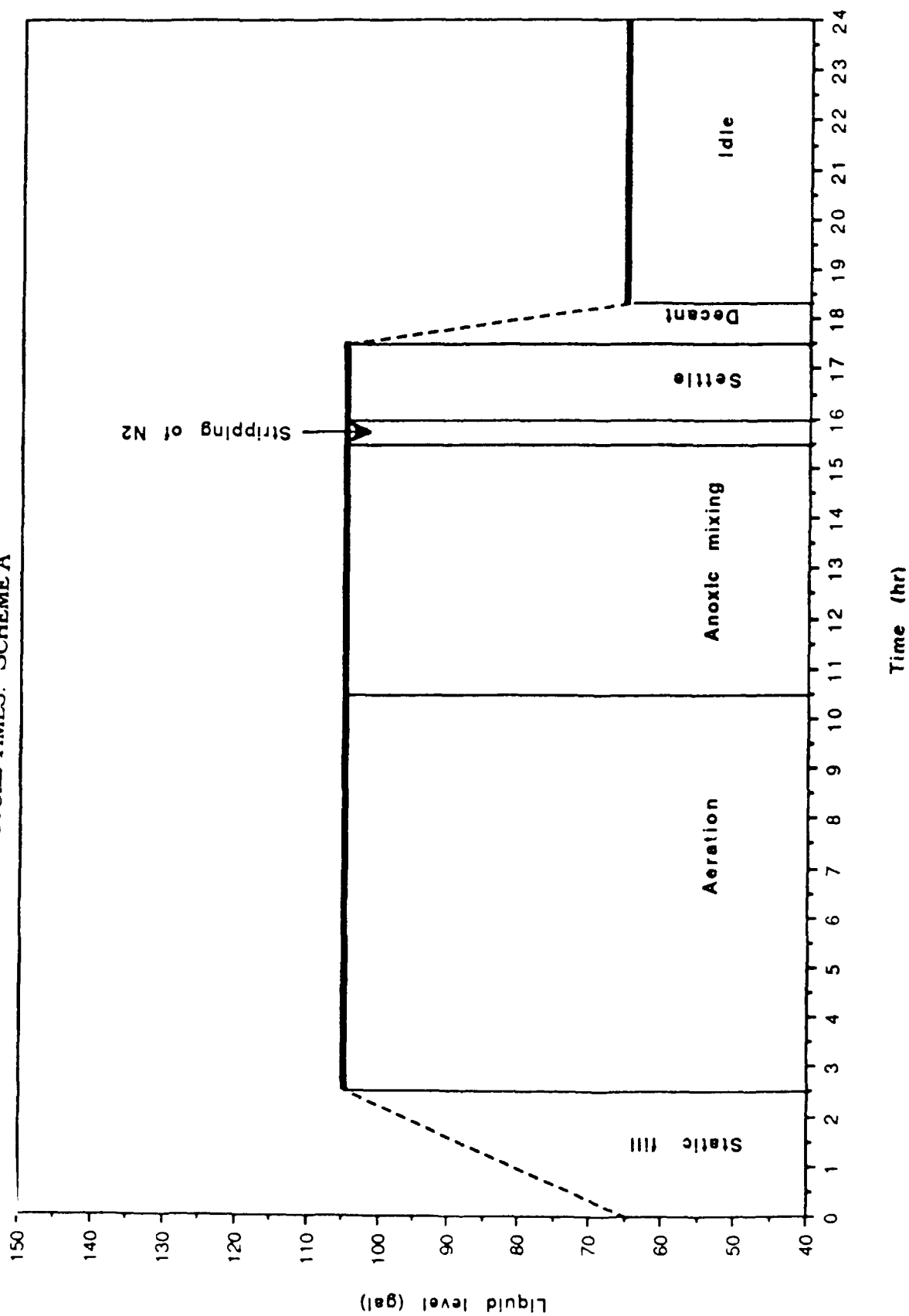


FIGURE 4: SBR CYCLE TIMES: SCHEME B

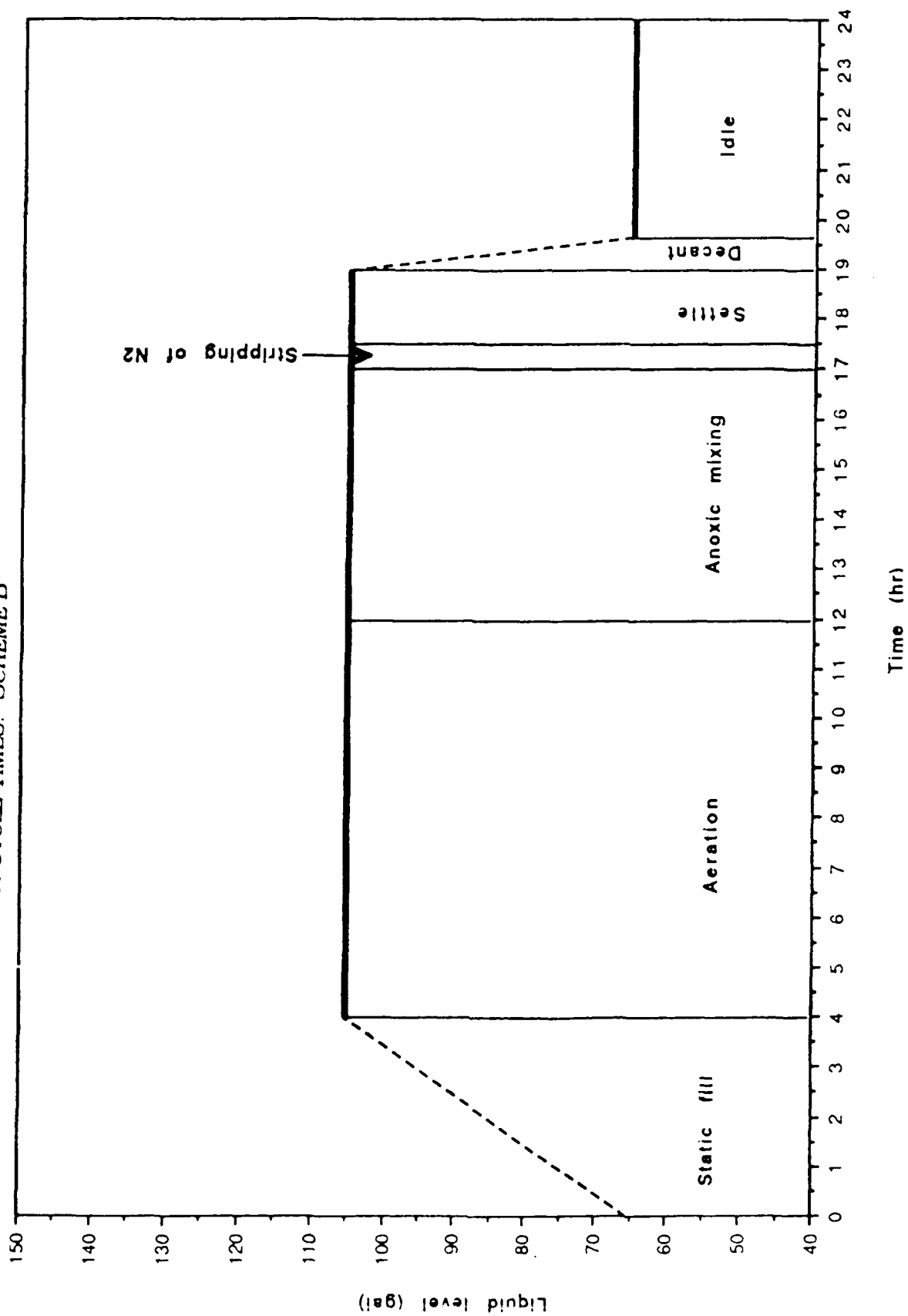


FIGURE 5: EFFLUENT BOD FOR SCHEME A AND B

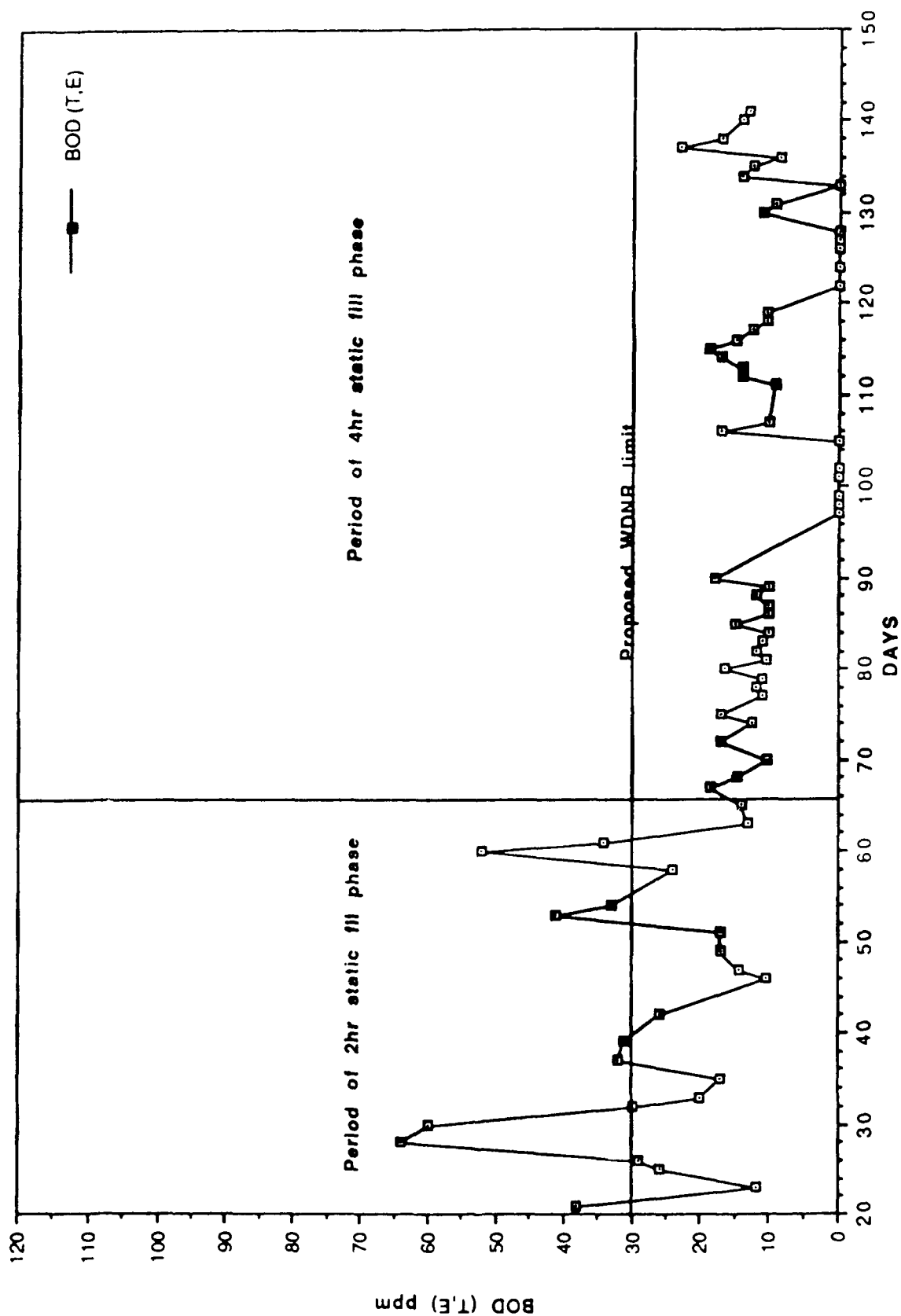


FIGURE 6: INFLUENT AND EFFLUENT NG CONCENTRATIONS

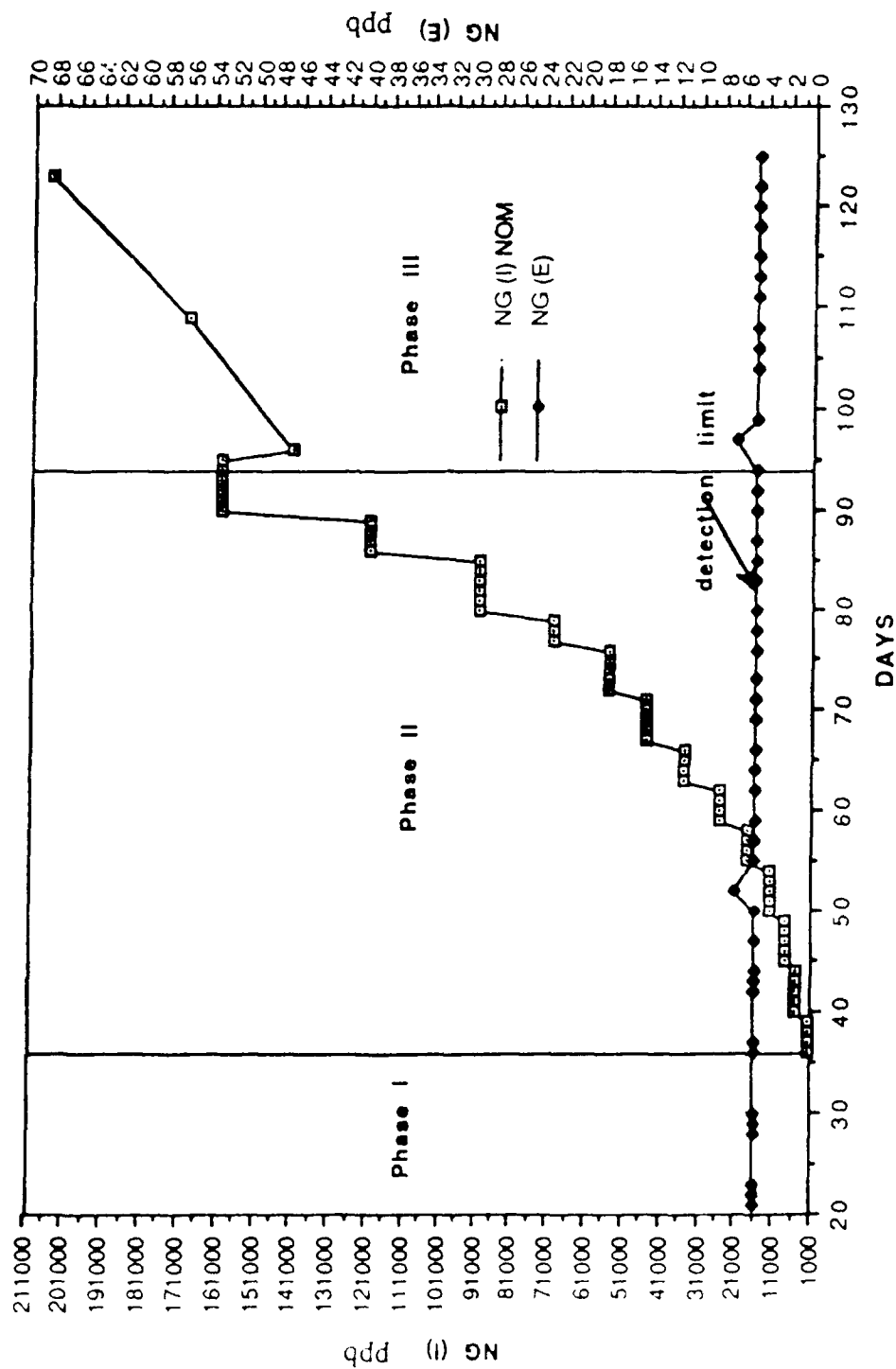


FIGURE 7: INFLUENT AND EFFLUENT $\text{NO}_3\text{-N}$ CONCENTRATIONS

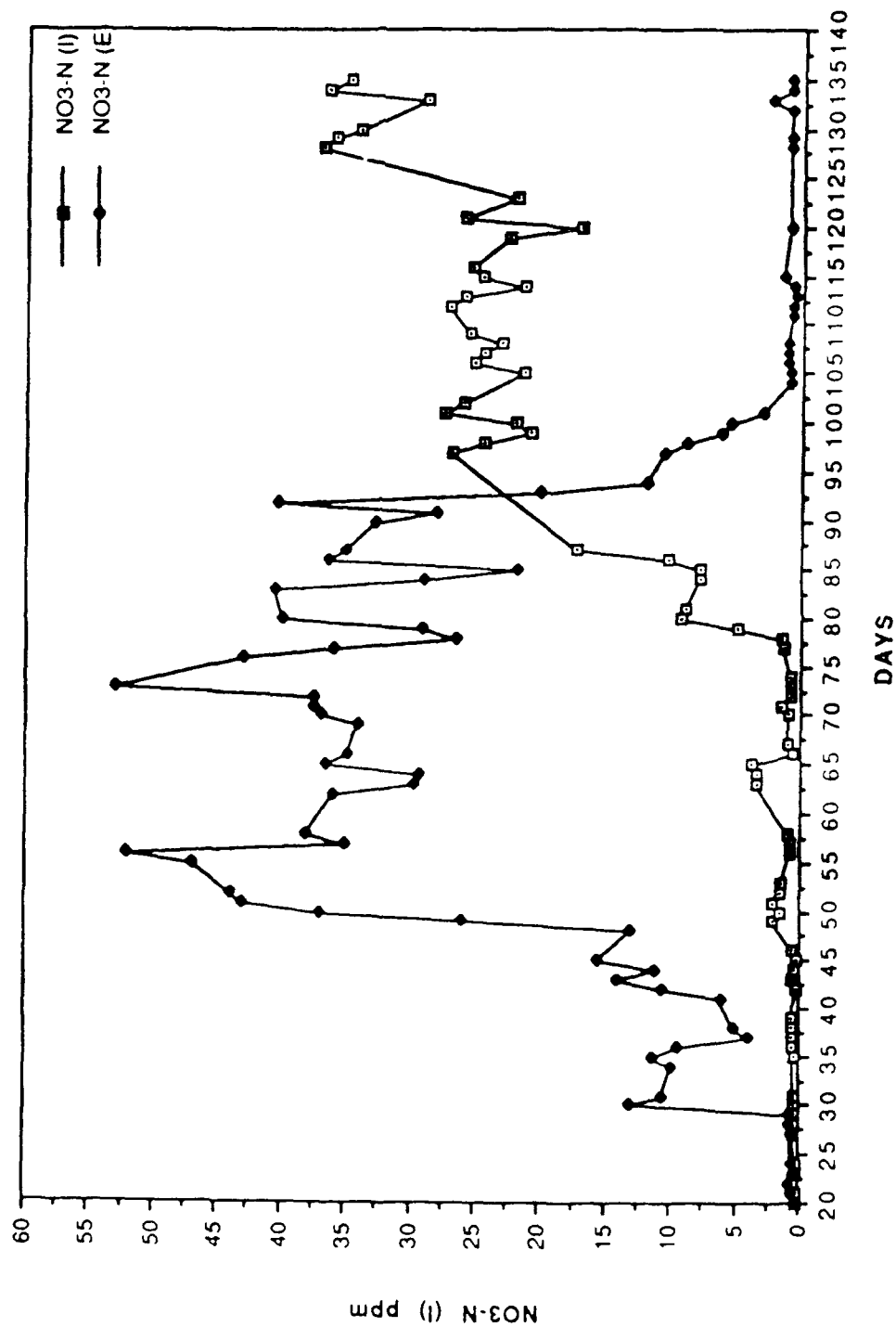


FIGURE 8: INFLUENT AND EFFLUENT DBP CONCENTRATIONS

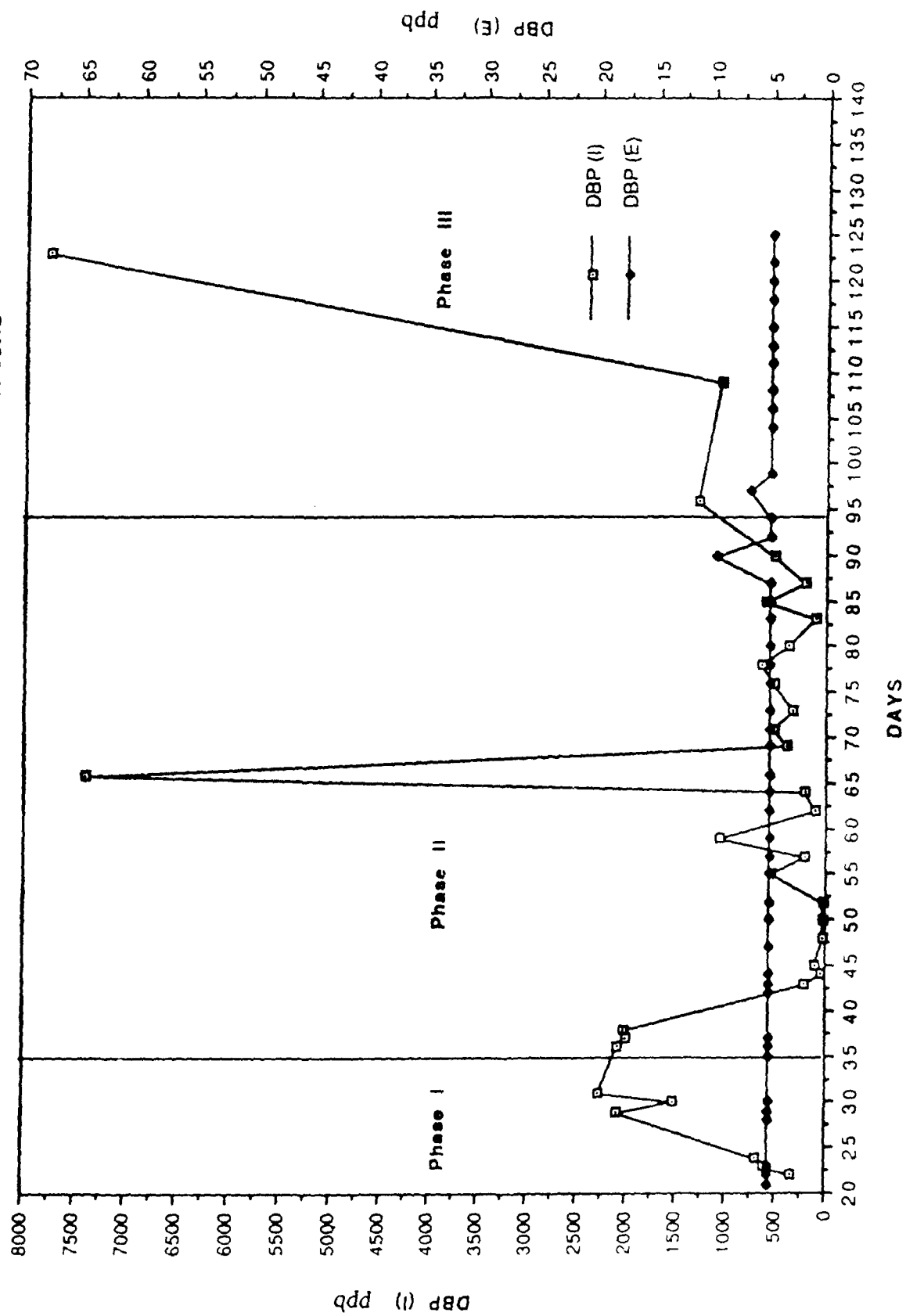


FIGURE 9: INFLUENT AND EFFLUENT DPA CONCENTRATIONS

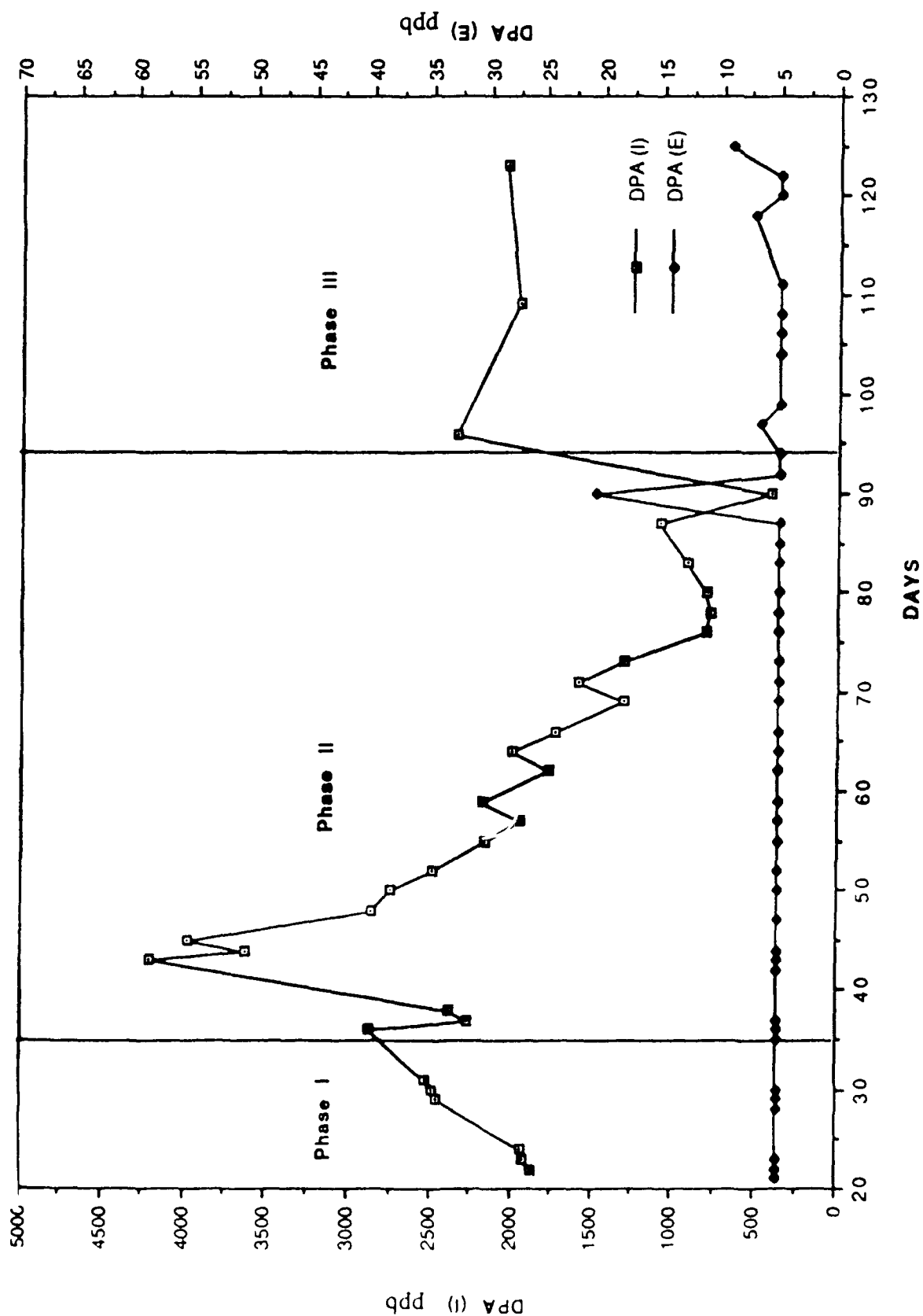
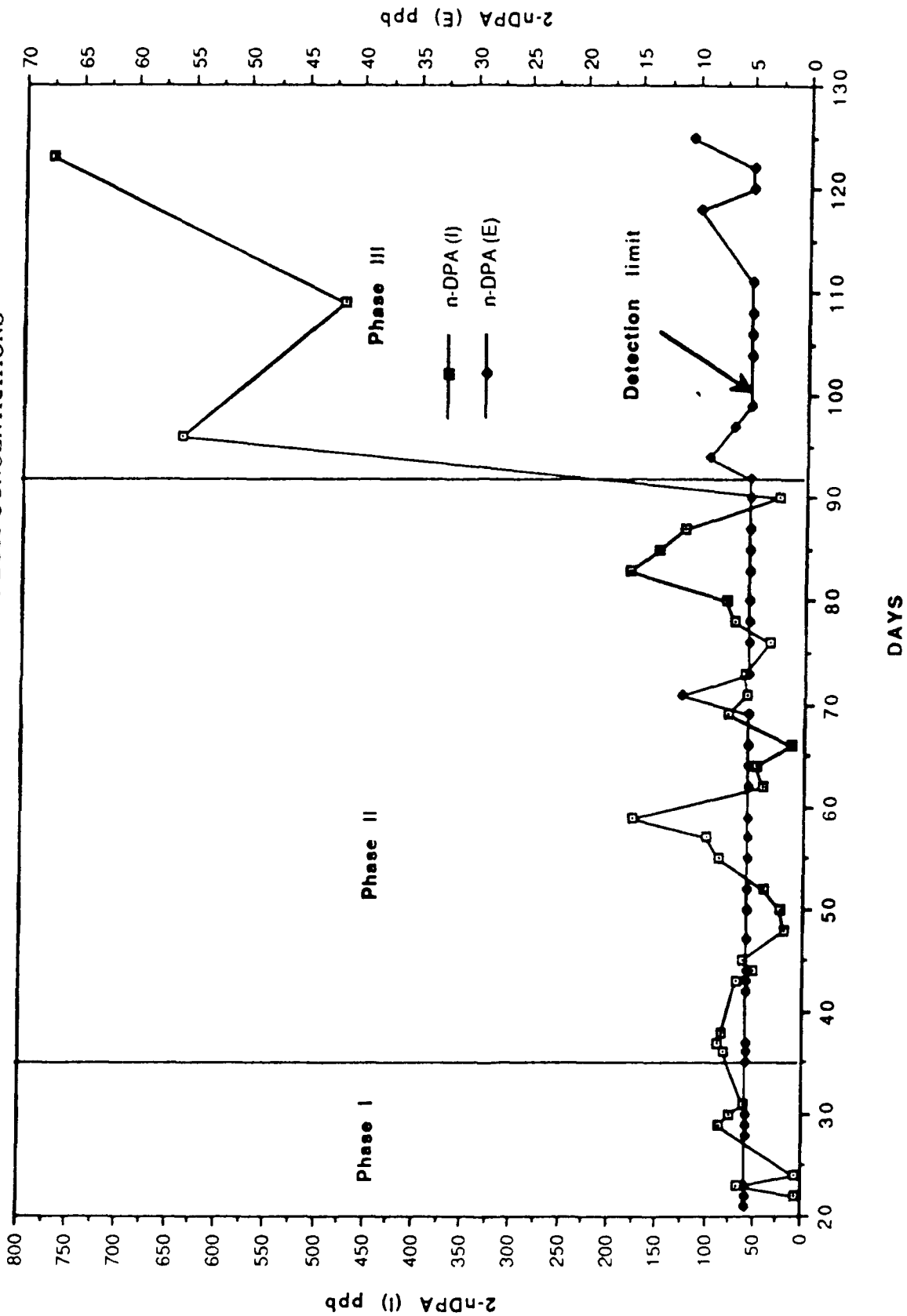


FIGURE 10: INFLUENT AND EFFLUENT NDPA CONCENTRATIONS



adversely impacted the removal of any of the other priority pollutants (DBP, DPA and nDPA).

COD and NG temporal reactor profiles are presented in Figures 11 and 12, respectively. As expected, the majority of the COD is removed within the first two hours of the oxic phase. Aqueous and biomass phase NG profiles indicate that it may be simultaneously sorbed and biodegraded (note: 5 ppm limit of detection for NG during this experiment). Moreover, given that the DO concentration in the reactor drops below 1 ppm after 15 minutes into the anoxic phase, it appears that NG may be amenable to anoxic, as well as oxic, biodegradation.

Typical results of bench scale studies utilizing the acclimated biomass and NG as the sole carbon source are presented in Figure 13. Only a 6% decrease in NG concentration was noted. This finding is in agreement with previous work [1] that reported a 9% decrease in NG concentration in shake-flask experiments in the absence of a primary carbon source. To further explore the issue of NG as a primary or cosubstrate, BOD assays were conducted on a variety of substrates. Figure 14 summarizes the results of BOD assays that utilized NG alone (100 ppm at various dilutions), EA alone (700 ppm) and NG and EA together (700 ppm EA and 100 ppm NG). The results illustrate that NG alone exerted no oxygen demand. Application of the Student t - test indicates that there is no statistical difference (0.05 level of significance) between the BOD exerted by the EA alone sample and the EA and NG sample. This confirms the bench scale results that indicate that NG can only be degraded as a cosubstrate. The consequences of these findings are of major significance. It is clear that if stable system performance is to be realized, a sufficient primary carbon source must be available in the influent to insure the cometabolism of NG. This may require the addition of an external carbon source to supplement the influent BOD, especially if NG concentrations become excessive.

SUMMARY

The work presented here was undertaken to investigate the feasibility of utilizing traditional biological unit operations to treat BP production wastewater laden with NG. Results indicate that biological cultures can be acclimated to treat NG - laden BP wastewater meeting all proposed discharge limits. NG can be degraded, as a cosubstrate, to below detection limits. Moreover, it appears that the removal mechanism for NG in a mixed culture oxic/anoxic system is simultaneous sorption and biodegradation.



FIGURE 11: REACTOR COD TEMPORAL PROFILE

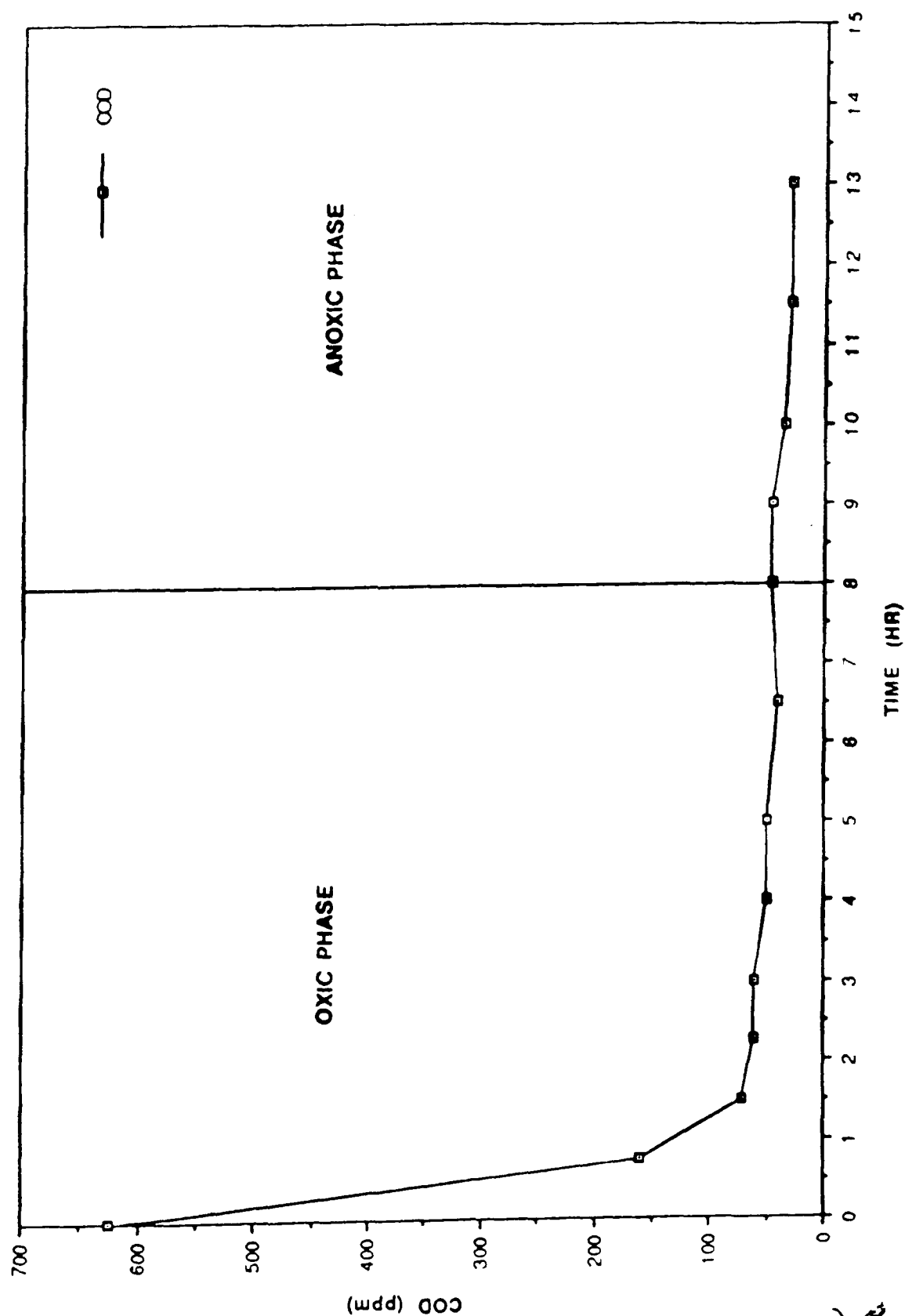


FIGURE 12: REACTOR NG TEMPORAL PROFILE

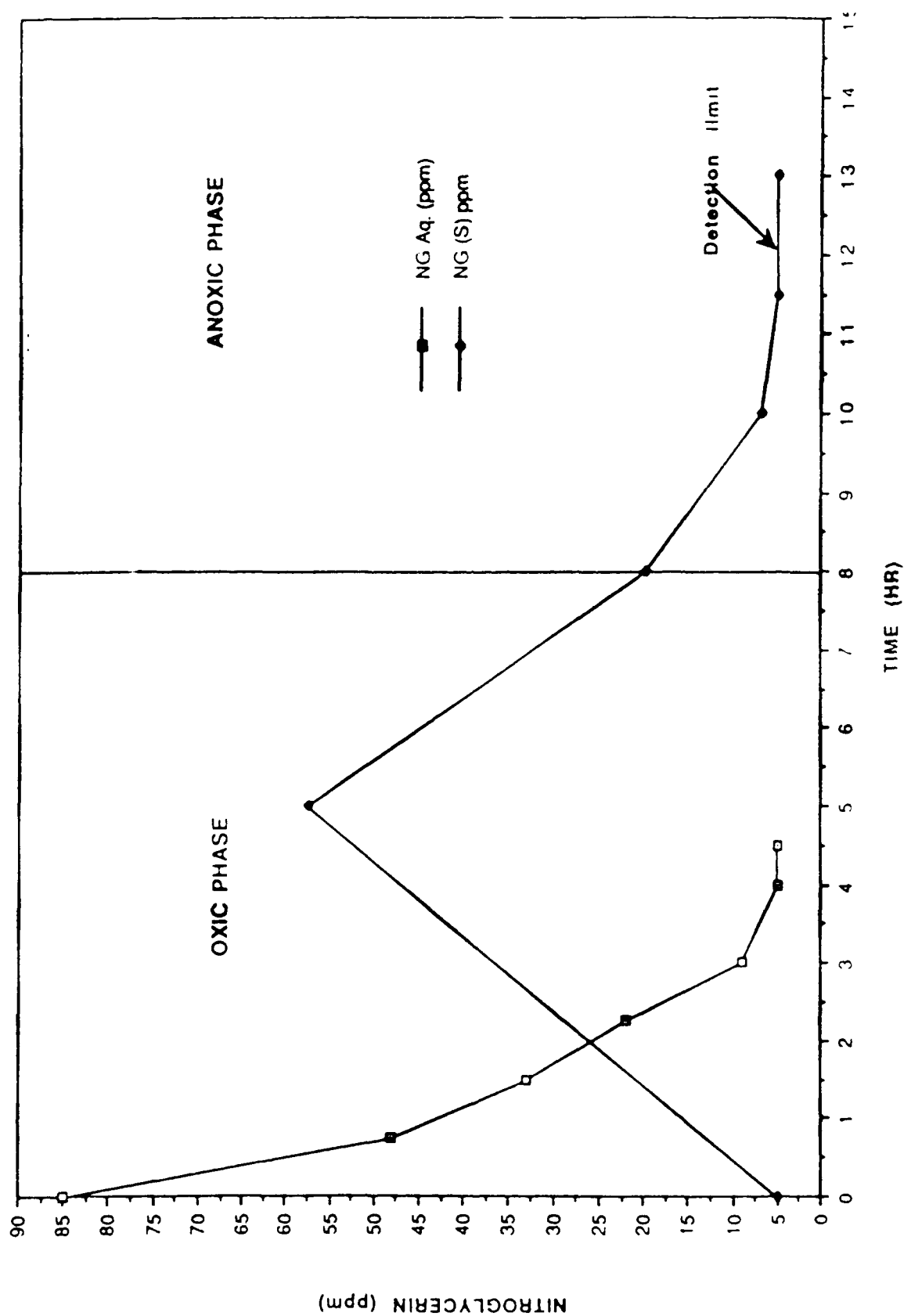


FIGURE 13: BENCH SCALE NG BIODEGRADATION STUDY

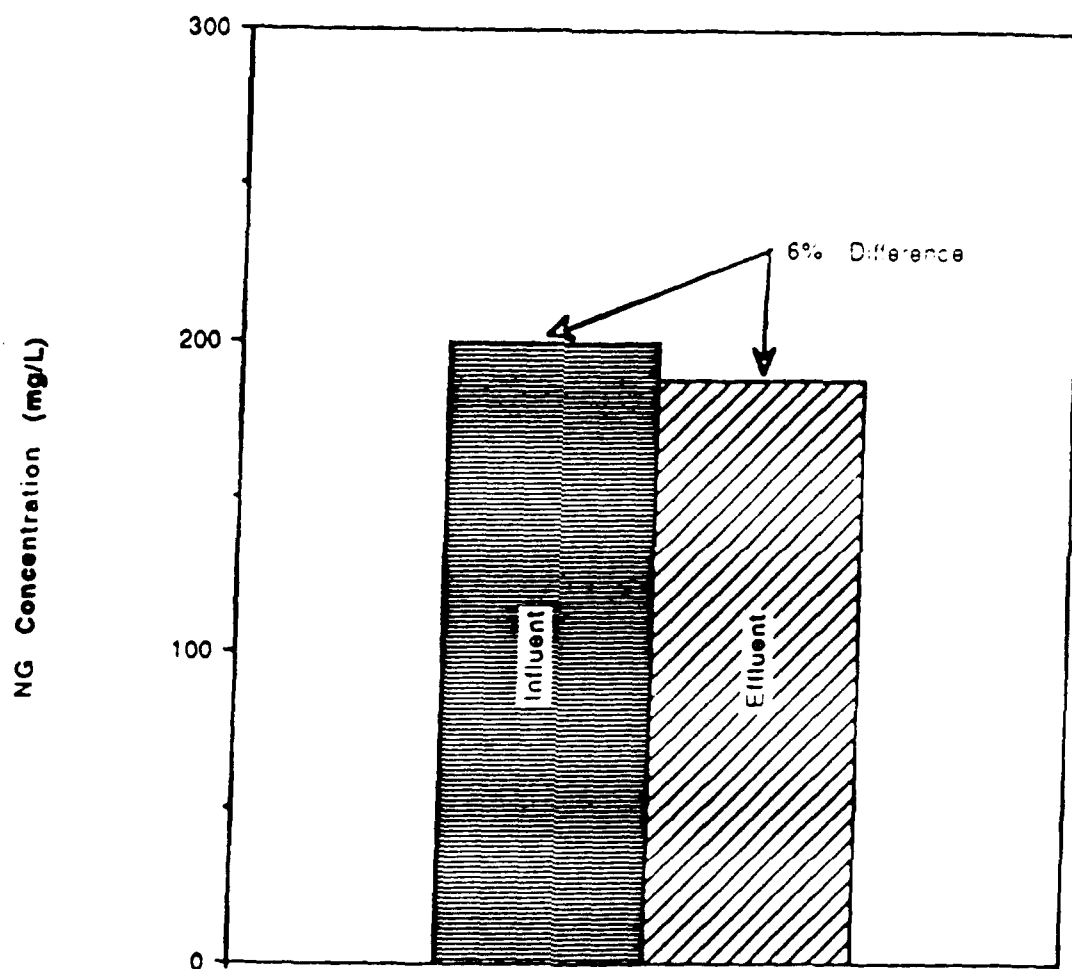
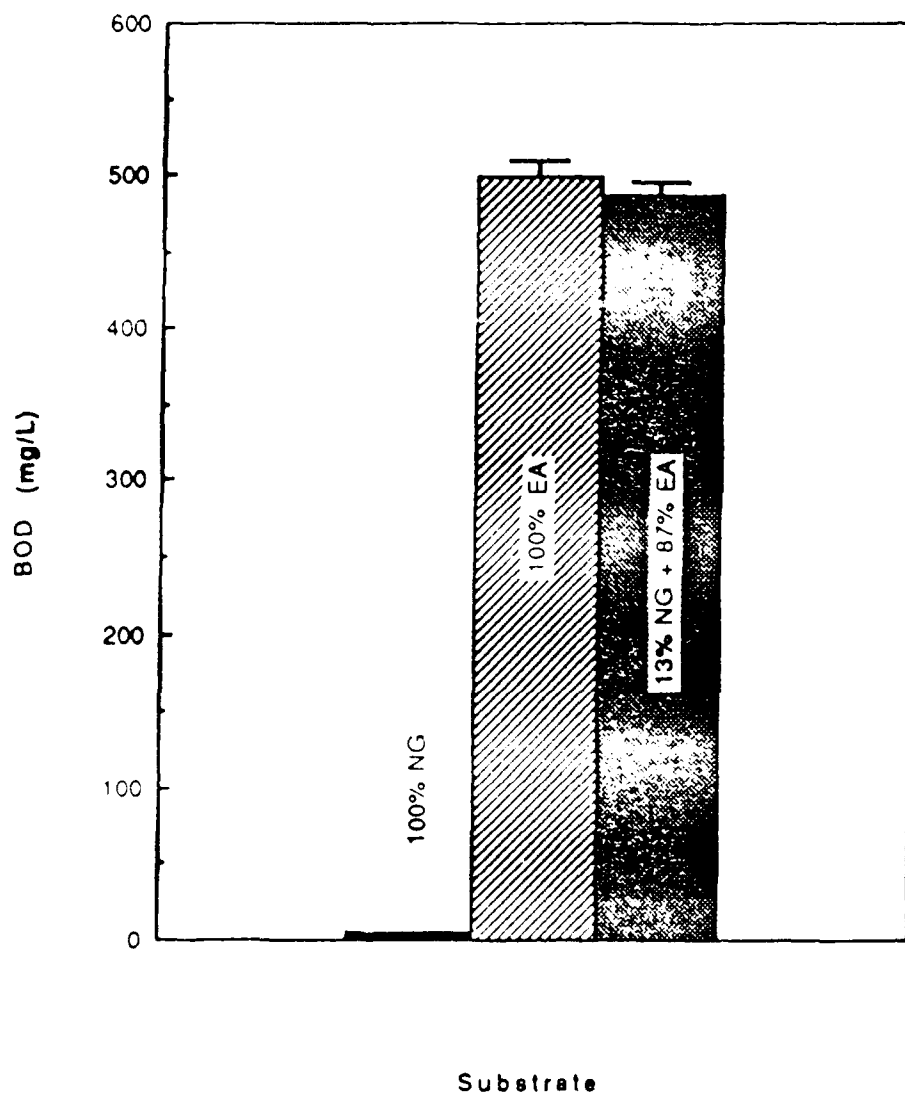


FIGURE 14: BOD ASSAY FOR VARIOUS SUBSTRATES



ACKNOWLEDGEMENTS

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Biodegradation of 2,4,6-Trinitrotoluene (TNT) Contaminated Soils in a Slurry Reactor

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ABSTRACT

Soils were obtained from Joliet Army Ammunition Plant (JAAP) and Newport Army Ammunition Plant (NAAP) to investigate the potential for utilizing a soil slurry biodegradation process as a remediation alternative. Soils obtained from JAAP were enriched for a microbial consortia capable of biodegrading TNT. The presence of a co-substrate was necessary in liquid and soil slurry cultures to achieve biodegradation. Malate and succinate have been utilized as co-substrates in laboratory studies conducted to this date. Approximately, 90% of the TNT was biodegradable, of this 10-15% of the TNT was converted to cell mass, and several metabolic intermediates. These intermediates have been identified (utilizing GC/MS) as 4-amino, 2,6,-dinitrotoluene and its isomer 2-amino, 4,6-dinitrotoluene. Prolonged incubation indicates that the consortia is capable of degrading these intermediates.

Laboratory scale soil slurry sequencing batch reactors (SS-SBR) were operated to investigate performance of a dynamic system. Laboratory reactors were operated utilizing different operating strategies. Reactor I was an aerobic system with malate as the co-substrate. This reactor reduced slurry TNT concentrations from 1500 mg/L to <3 mg/L in 13 days. Reactor II was an anoxic (no added oxygen, nitrate as the electron acceptor), and malate as the co-substrate. This reactor reduced slurry TNT concentrations from 1500 mg/L to <3 mg/L in 15 days. Reactor III was an anoxic reactor (utilizing nitrate as the electron acceptor) with succinate as a co-substrate. TNT concentrations were reduced from 1400 mg/L to <3 mg/L in 20 days. Soils obtained from NAAP (which was heavily contaminated with TPH) did not have the biological capabilities to degrade TNT in a SS-SBR. NAAP soils when inoculated with organisms from a JAAP reactor and organisms from a diesel fuel reactor, TNT reductions of 78-90% were observed after 12 days. These laboratory treatability studies demonstrated the promise of utilizing biodegradation to treat soil contaminated with TNT.

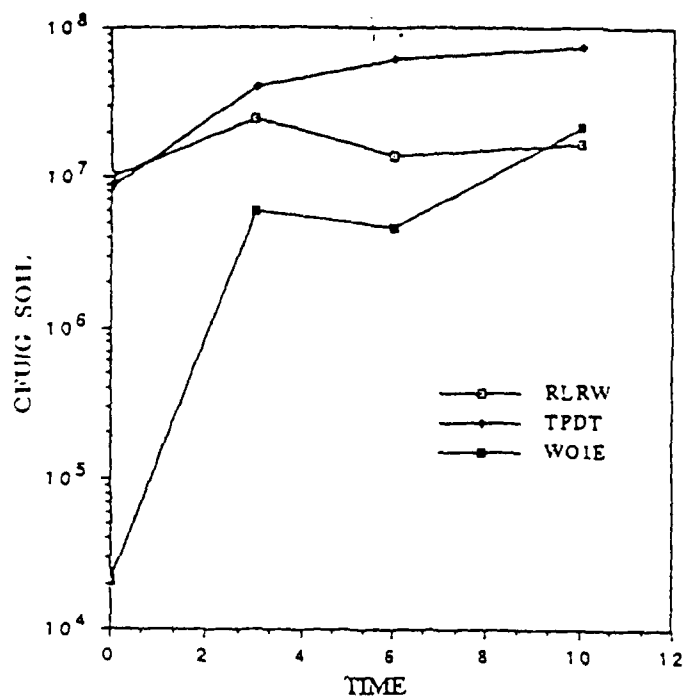


Figure 1. Microbial Growth Analysis of Selected Soil Samples from Joliet Arsenal. Growth media was nutrient agar. All samples were from TNT contaminated areas of the Joliet Arsenal.

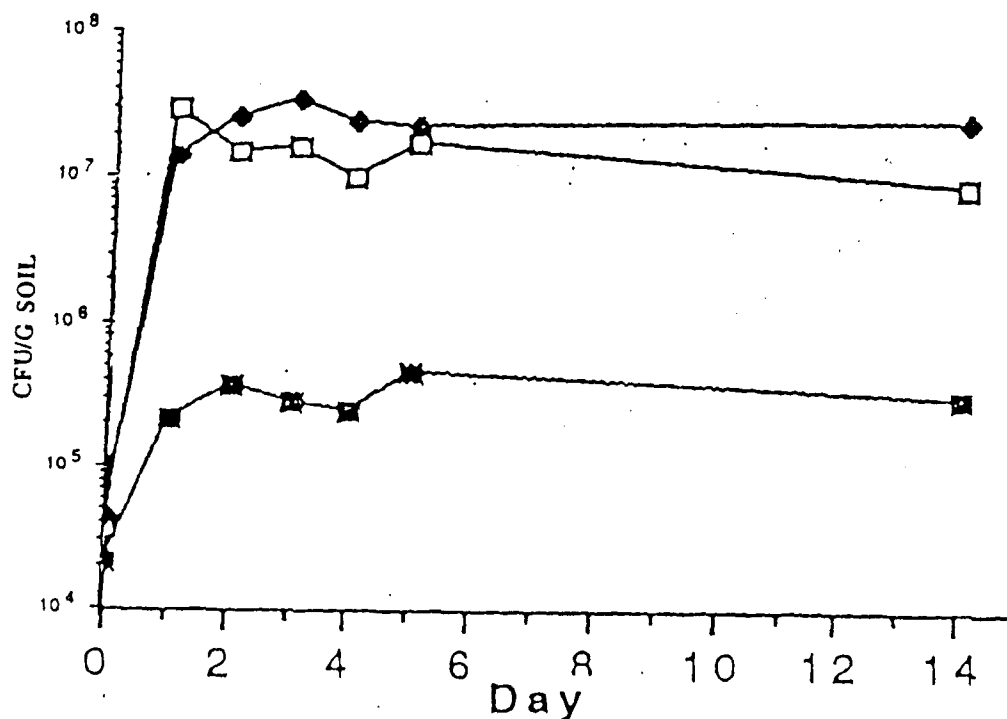


Figure 2. Growth of RLRW consortium with and without TNT and/or succinate.
 RS+S: RLRW consortium + succinate + TNT □
 RS+S w/o TNT: RLRW consortium + succinate ♦
 RS: RLRW consortium w/o succinate. ■



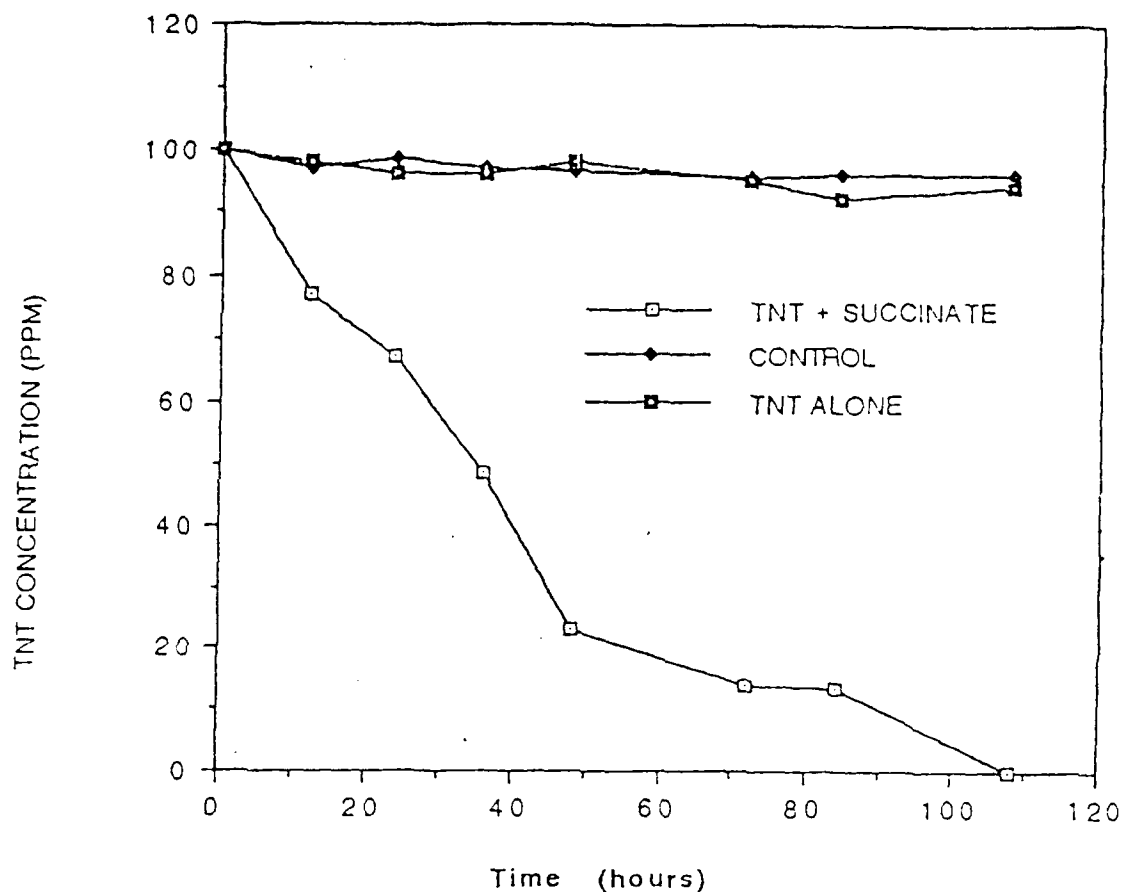


Figure 3. Shake flask study of the Disappearance of TNT
 TNT alone: RLRW consortium + TNT
 TNT + Succinate: RLRW consortium + Succinate + TNT
 Control: Autoclaved RLRW consortium + TNT + Succinate

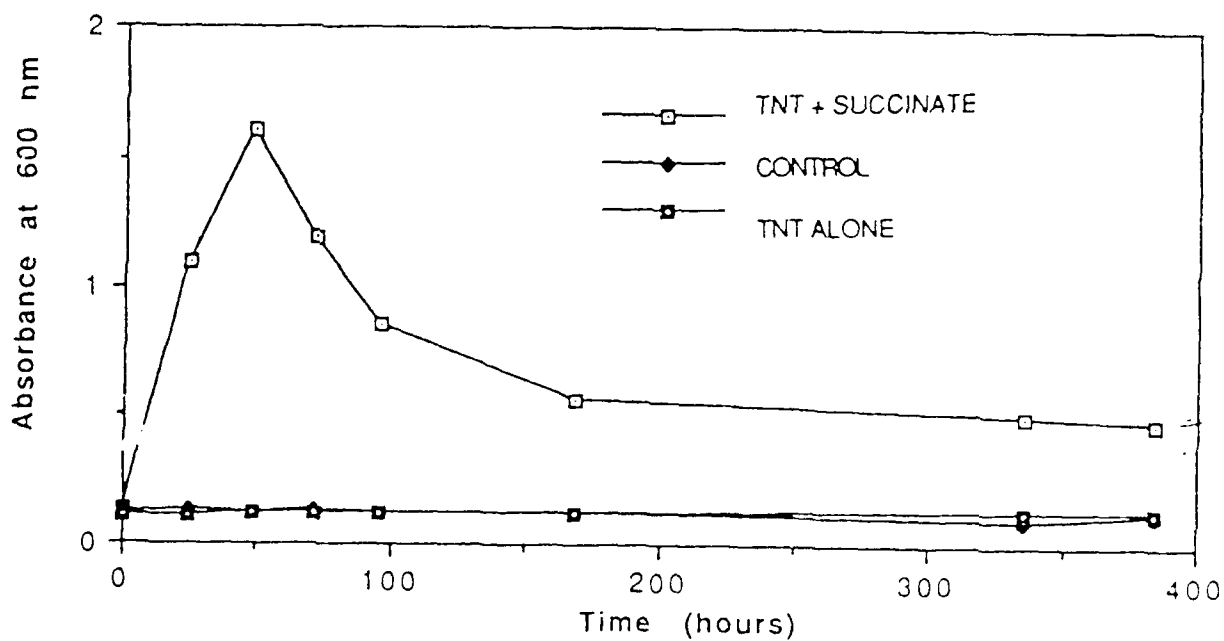


Figure 4. Growth Curve of RLRW consortium
 Flask contents are identical to Figure 3

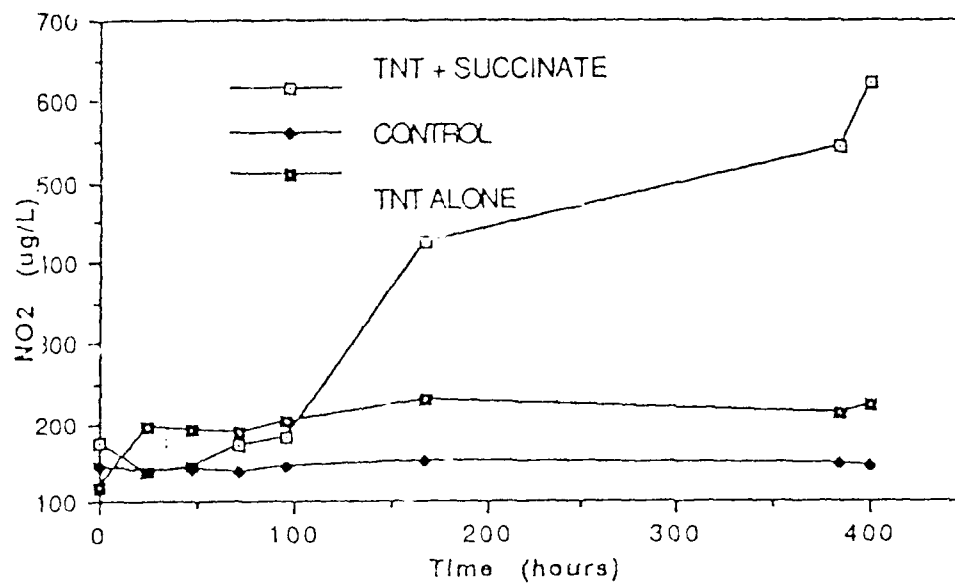


Figure 5. Production of Nitrite by RLRW consortium
Flask contents are identical to Figure 3.

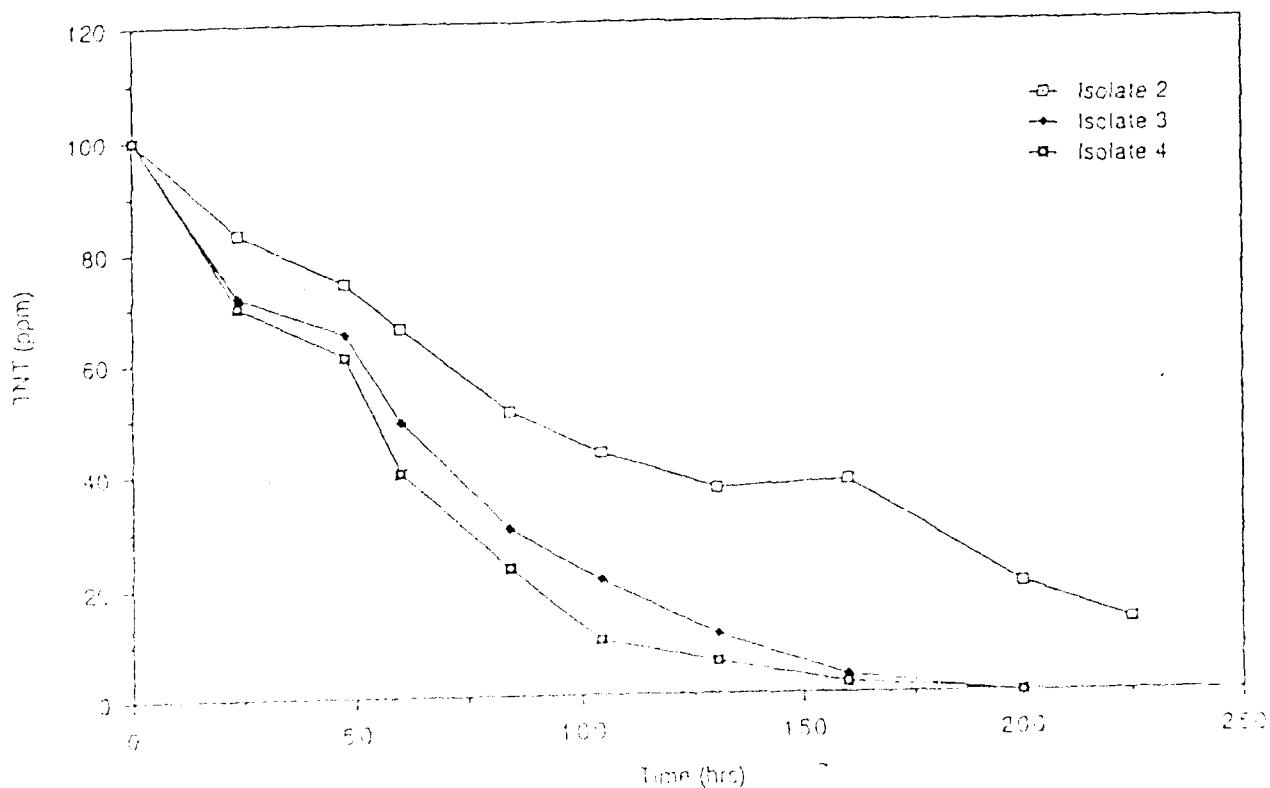


Figure 6. Pure culture biodegradation of TNT.

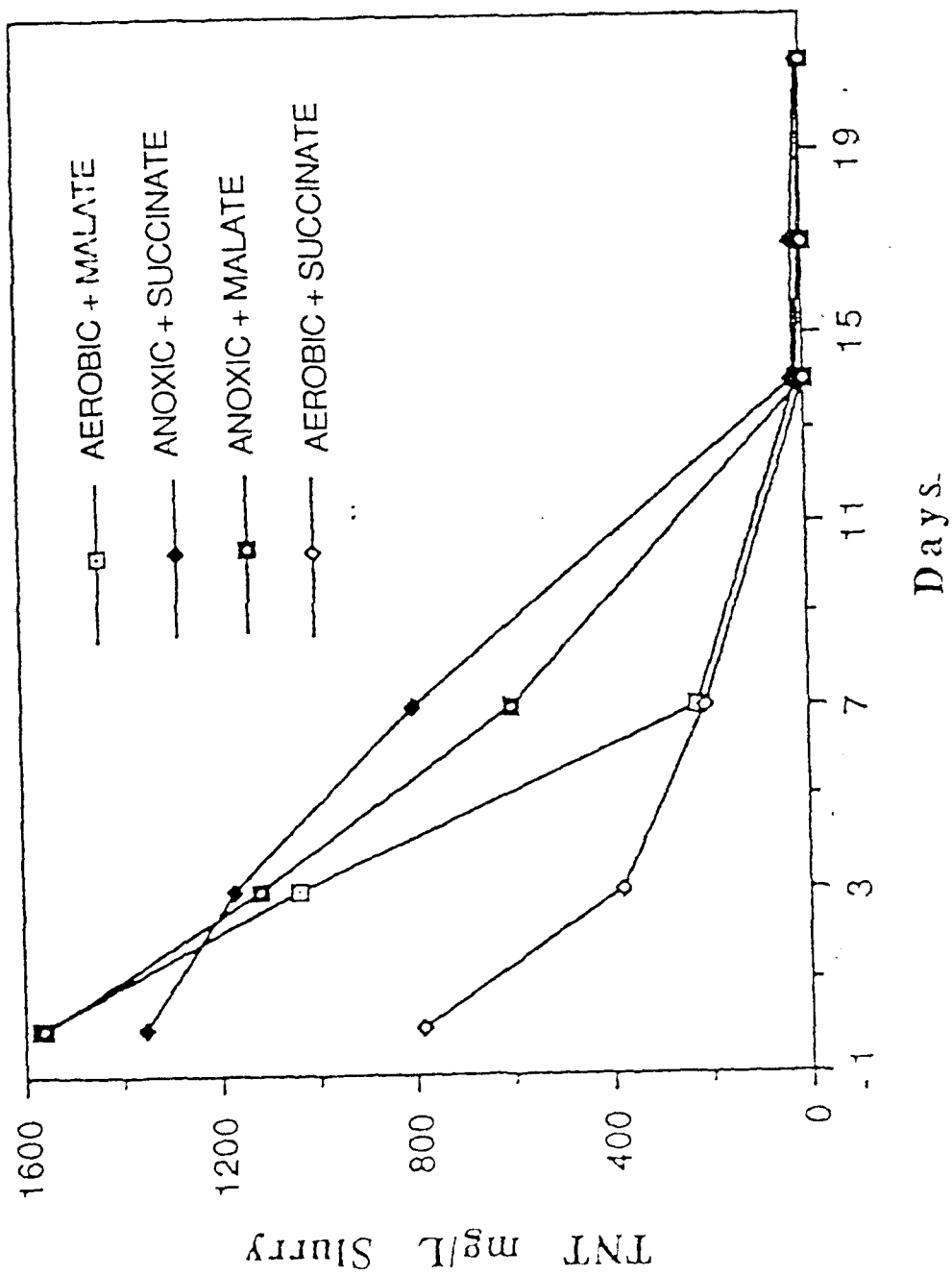
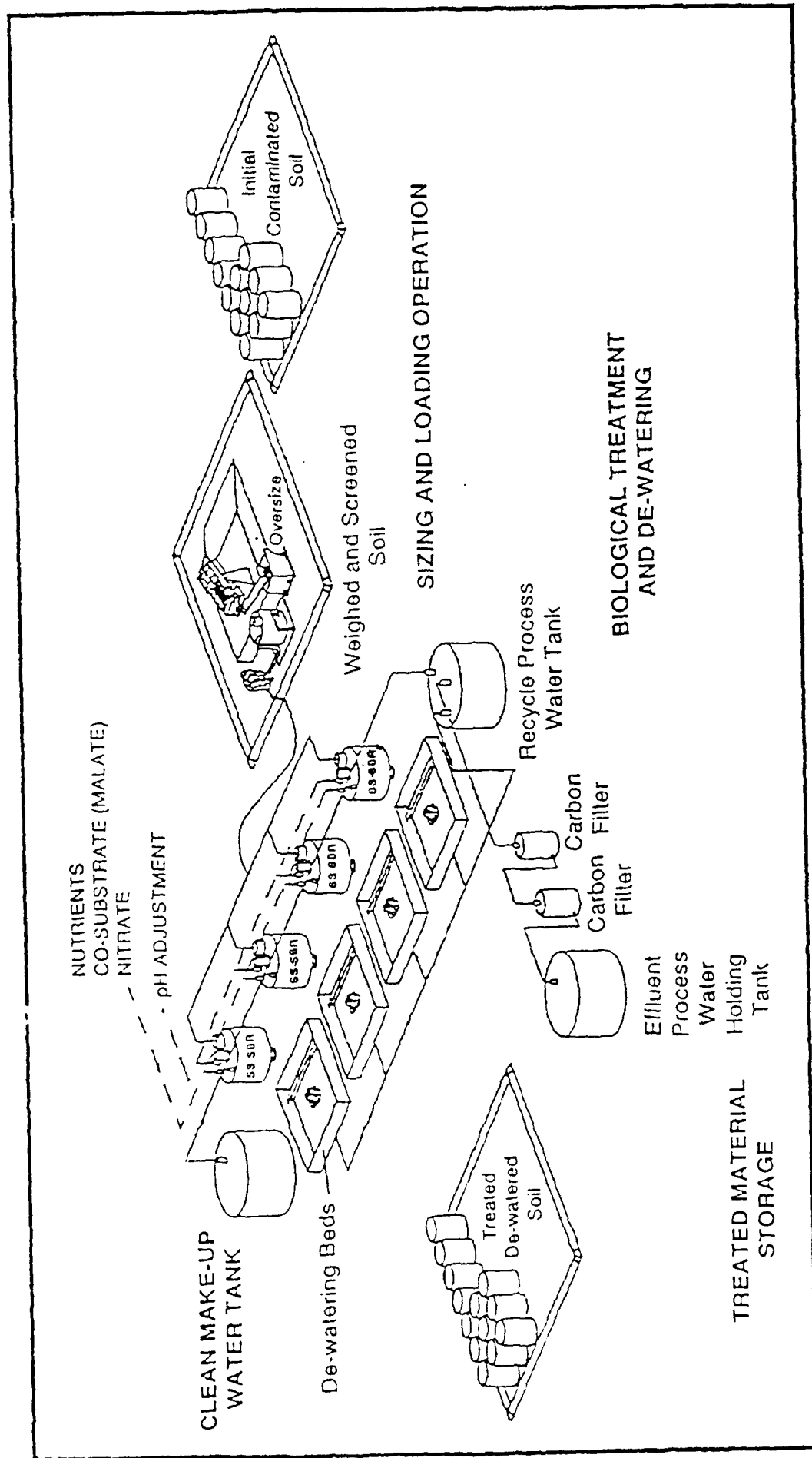


Figure 7. Soil Slurry Reactors Degradation of TNT.

Figure 8. Proposed Pilot Scale Soil Slurry Reactor

BIOREMEDIATION FLOW DIAGRAM



SEQUESTER OF ZINC, COPPER, CADMIUM, AND MANGANESE WITH A MIXED MICROBIAL MAT SYSTEM

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ABSTRACT

The objective of this research was to investigate the metal-sequestering potential of a mixed microbial mat ecosystem. Initially, strains of bacteria and cyanobacteria were developed for tolerance to the specific metals targeted for bioremediation strategies. Separate cultures of these strains were integrated into a mixed microbial mat by inoculating the metal-tolerant microbes in laboratory ponds enriched with ensilaged grass clippings. In 7-10 days, the natural microbial dynamics in the pond spontaneously produced a gelatinous mat composed predominantly of cyanobacteria. This mat was further adapted to the metal-contaminated water by step-wise exposure to increasing concentrations of the target metal solutions. Excised sections of the mature metal-tolerant mats were applied to contaminated samples from mine drainage water containing Zn, Cu and Cd in concentrations (mg/L) of 3250, 279 and 28, respectively. A 27-day water treatment with excised mats resulted in the following decreases in metal concentrations: Zn = 87% Cu and Cd = 99%. In order to increase the rate of metal removal, mats were immobilized on glass wool and anchored in a flow-through baffle system. Ten flows of Cd-contaminated water (0.5 L of 20-22 mg/L Cd) resulted in an average Cd uptake of 94% with a flow rate of 2.5 ml/min. Four flows of a mixed solutions of Zn and Mn (0.5 L each, concentrations in mg/L: Zn = 16; Mn = 13) resulted in 99% removal of both metals. When immobilized on glass fiber, the cyanobacteria mats proved to be a rapid and effective system for bioremediation of metal-contaminated water. These mats were found to be resilient and highly predictable in terms of ecological behavior and metal sequestering.

INTRODUCTION

Mixed microbial mats, composed of stratified layers of bacteria and cyanobacteria, often occupy the most inhospitable environments on earth. Photosynthetic microbes, which generally dominate this unusual niche, are the highly tolerant cyanobacteria, which fix both carbon and nitrogen. A laminated multi-layer of facultative, heterotrophic bacteria and anoxygenic photosynthetic purple bacteria colonize below the cyanobacteria photozone. The final stable community constitutes a highly diverse, mixed microbial ecosystem. Metal-tolerant mat ecosystems, because of their resilience and functional diversity, may bring a flexibility and efficiency to biotechnology that is frequently lacking in single species systems.

Earlier research demonstrated that microbial mats can be rapidly cultured by using ensiled grass clippings as a substrate and easily developed for tolerance to a variety of metals (Bender et al., 1989a,b). These ecosystems are self-organized and grow with a predictable pattern of succession. Mats, adapted for metal resistance, are generally effective in sequestering these metals from their environments (Bender et al., 1989a). The objective of this research was to explore two bioremediation technologies with the metal-tolerant microbial mats: (1) capacity of excised sections of mat to reduce metals in mine drainage, and (2) uptake potential of immobilized mat systems in the sequester of Mn, Cd, Cu and Zn.

METHODS

Mat development for metal sequestering. Mats were developed in laboratory ponds, cm: 15 x 12 x 11. The pH was self-maintained at 7-8. Ensiled grass clippings (0.9 g/pond, dry wt), prepared according to the procedures of (McDonald, 1981), provided nutrients and substrate for attachment. Metal-tolerant mats, developed in earlier research (Bender, 1991), were added as inocula. Mats were cultured in an environmental chamber with day/night (12 h light: 12 h dark) illumination. In the baffle experiments, both top and bottom of the tanks were illuminated to produce cyanobacteria growth on all surfaces. Mats were harvested from the

ponds and used in the following ways: (1) excised sections were added to samples of Iron Mountain Mine drainage containing Zn, Cd and Cu, and (2) desiccated mat inocula were added to the glass wool matrix, which was then layered in a baffle tank for flow-through treatment of Cd, Zn and Mn solutions. This provided an immobilized cell system of mat in which the various species of bacteria self-organized on the filaments of glass wool beneath the surface cyanobacteria stratum. Silage/soil wash (SSW medium) was used to periodically enrich the mature mats in the baffle and also to dilute the mine drainage sample in the excised mat experiments. SSW was prepared by washing 2 L soil, pH 7-8, and soaking 7 g (dry wt) of ensiled grass in the wash. The following mineral additions were made (μL): K_2PO_4 (2), KH_2PO_4 (3), K_2CO_3 (2), CaCO_3 (5). Samples (before and after treatment) were hydrolyzed and analyzed for metal concentration by atomic absorption (APHA, AWWA, WPCF, 1985).

Excised mat experiment. Sections of metal-tolerant mat (9 cm^2) were excised and added to 200 ml solutions of mine drainage sample diluted (1:1) with SSW medium. Solutions contained the following concentrations (mg/L) of Zn, Cu and Cd, respectively, 3250, 279 and 28. Water columns were sampled periodically, hydrolyzed and analyzed for the three metals.

Baffle experiment. Acrylic baffle tanks (61 x 16 x 16 cm, containing 5 baffles) were designed to produce a slow, "S" flow path of the metal solution through the system. Tank bottoms were layered with 3 cm of glass wool, 11 g ensiled grass clippings and flooded with 0.8 L nutrient (SSW) medium. Metal-tolerant mat inoculum was crushed and scattered in the wool layer. After the cyanobacteria began to grow it migrated to the illuminated region, thereby colonizing the outer surfaces of the wool layer. To maintain cellular attachment, SSW was added periodically. Ten flows (0.5 L each) of Cd solution, containing 20-22 mg/L, were passed through the system. In separate baffle tanks, four flows (0.5 L each) of Zn-Mn mixed solution, containing 16 mg/L Zn and 13 mg/L Mn were passed through the immobilized mat system. Input and exit solutions were hydrolyzed and measured for metal concentrations. In order to compare metal-uptake potential of live mats compared to dead cell mats, the glass wool/mats were removed from the baffle tanks, heat sterilized and replaced. Subsequently, metal solutions were passed through the system and the effluents were analyzed for metal concentrations.

RESULTS AND DISCUSSION

Zn, Cd and Cu sequester from Iron Mountain Mine drainage using excised mats. Figure 1 shows the exit of the three metals from the mine drainage solution in a 27-day treatment period. Mat blanching, followed by deposits of slime material around the mat indicated some cell death. However, mats retained some green color and macrostructure throughout the experiment. Although the high levels of metal uptake, Zn: 87%, Cu and Cd: 99%, indicate good decontamination of the water column, the required treatment time was too long to be considered a feasible remediation strategy. In order to increase the metal sequester rate, mats were immobilized on glass wool and layered in a flow-through baffle tank.

Metal uptake in the mat/baffle system. Figure 2 shows the Cd sequester by the mat in the immobilized cell system. The total Cd removed from the contaminated water in the ten flows was 96.8 mg, representing an average removal of 94.3%, with a flow rate of 2.5 mL/min. After ten flows of Cd solution (5 L of 20-22 mg/L), no significant cell death was apparent in the mat. As the number of Cd flows increased, black spots appeared on the mat surfaces. Flooding with SSW medium overnight produced a new growth layer over the black deposits. Although the mechanism of metal transport and deposit by this immobilized mat system is not known, the appearance of black spots on the surface mat, as the Cd solution flowed through the interior of the glass wool, indicated that some of the Cd was initially deposited on the cyanobacteria surfaces. After several days the spots disappeared from most of the mat surface area. Subsequent analyses showed that the final location of metal storage was below the cyanobacteria region.

In the case of Zn and Mn the flow rate was increased to approximately 15 mL/min. Figure 3 shows that the simultaneous uptake of Zn and Mn in the mat/baffle system was 99% for each metal in four flows. Uptake in the control tanks (containing only glass wool) was insignificant.



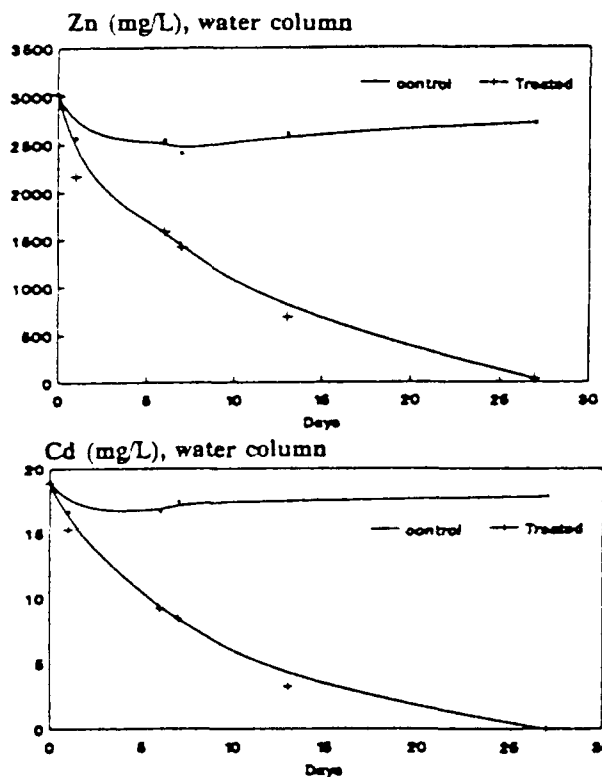


Figure 1. Sequester of Zn, Cd and Cu from mine drainage with excised sections of microbial mat.

Control: mine drainage water diluted 1:1 with nutrient medium; no mat added.

Treated: mine drainage water diluted 1:1 with nutrient medium plus mat ($9 \text{ cm}^2 / 0.2 \text{ L}$).

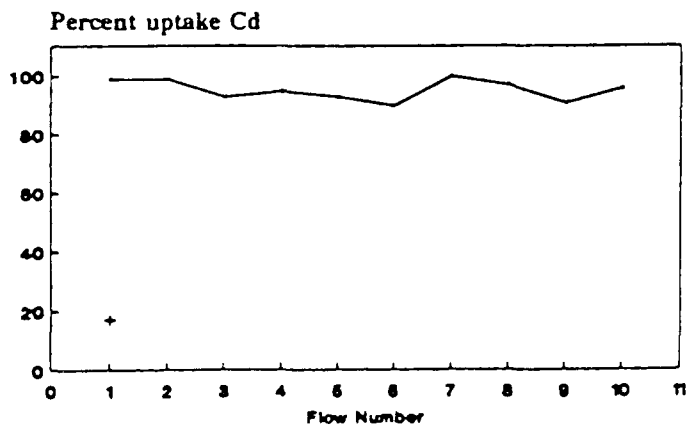


Figure 2. Cadmium uptake by immobilized mat in a flow-through baffle.

Experimental baffle tank (■) contains mat immobilized on glass wool; Control (+) contains glass wool only. Input = 10 flows of 0.5 L, 20-22 mg/L Cd.

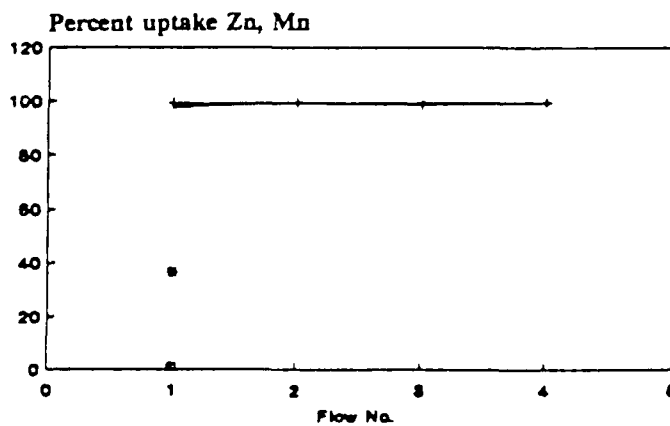


Figure 3. Simultaneous uptake of zinc and manganese by immobilized mat in a flow-through baffle.

Experimental baffle tank (■) contains mat immobilized on glass wool; Control (+) contains glass wool only. Experimental Zn (■); experimental Mn (+); control Zn (●); control Mn (□). Input = 4 flows of 0.5 L, Zn: 16 mg/L; Mn: 13 mg/L.

Metal uptake with live and dead cells. Heat-killed mats (figures 4 and 5) showed a somewhat lower uptake and much greater variability among the flows than did the live mats. It is not known whether the effectiveness of the live mat was due to the function of active transport or whether the cellular attachment to substrate surfaces (absent in the dead mat) produced a complex labyrinth in the flow path, which both increased cell surface exposure as the solution passed through the tank. Further experiments in defining these process are currently in progress.

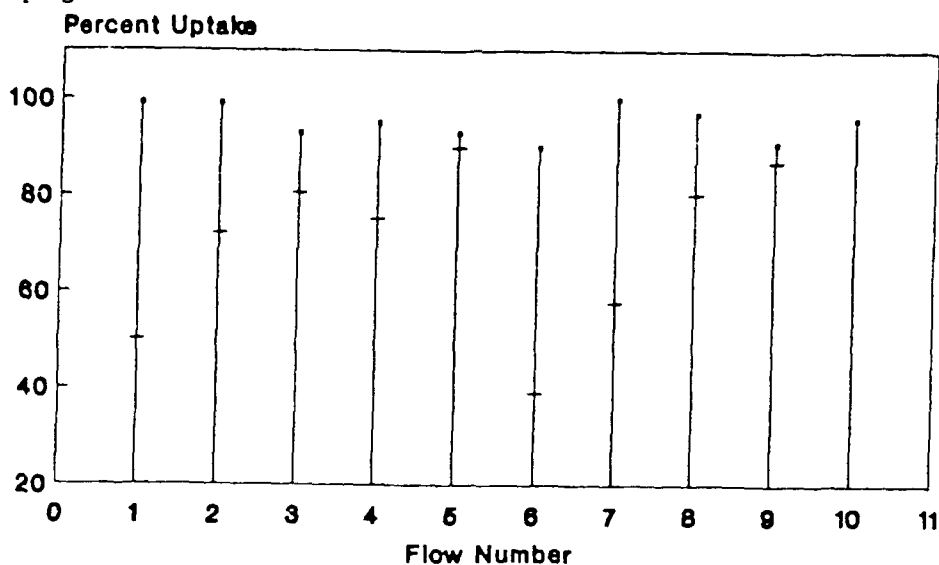


Figure 4. Cadmium uptake comparing live mat to heat-killed.

Mats immobilized on glass wool in a baffle tank.

Live mat (■); heat killed (+).

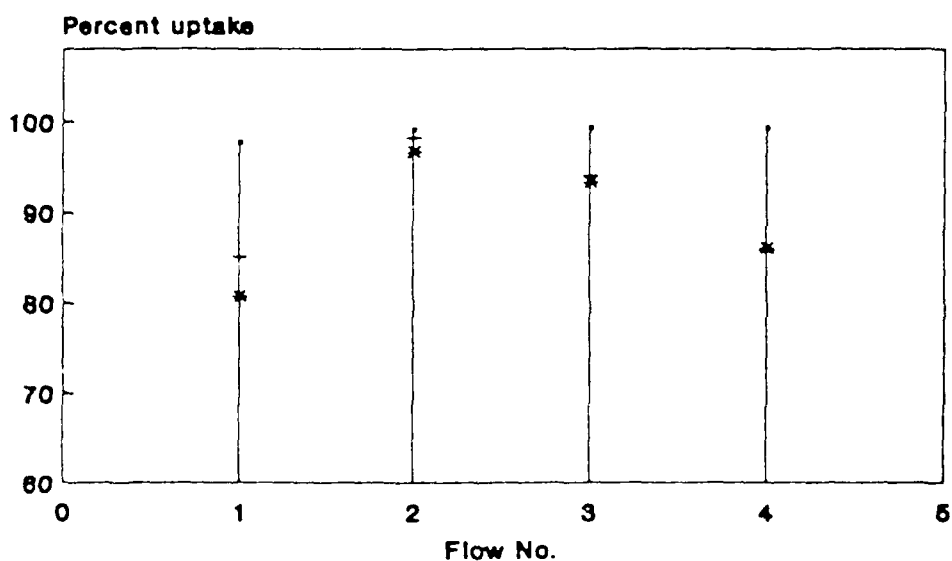


Figure 5. Zinc and manganese uptake in live mats compared to heat-killed.

Mats immobilized on glass wool in a baffle tank.

Ave. Zn and Mn uptake by live mat (■);

Zn (+) and Mn (*) uptake in heat killed mat.



Additions of concentrated HCl to samples of the metal-exposed mat produced a distinct odor of H₂S, indicating that a pool of sulfide ions are available for metal precipitation in or near the mat. Earlier research confirmed that lead, sequestered by mats in small laboratory ponds, was deposited as PbS (Bender et al., 1989a). The sulfide pools, characteristically associated with mats, may result from the metabolic activities of sulfur-reducing bacteria residing in the anaerobic zones below and within the mats (Cohen, 1989). Species of sulfur reducers have been identified in our mats (Archibold et al., 1989).

The mixed microbial mats, generated with ensiled grass clippings, are durable, self-organizing ecosystems, which have few growth requirements. Since they are dominated by photosynthetic and nitrogen-fixing microbes, they essentially provide their own nutrient supply and remain viable in the water column or attached to inert substrates for extended periods of time. Their tolerance to toxic materials, ability to effectively decontaminate their environment and capacity for metal storage without cell death demonstrates high potential for low-cost bioremediation strategies.

ACKNOWLEDGEMENTS

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A WASTE MINIMIZATION CASE STUDY AT A U.S. ARMY METAL PARTS MANUFACTURING FACILITY

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INTRODUCTION

It is United States Army policy to reduce the volume and toxicity of hazardous waste generated by Army operations and activities to the extent that is economically practical and environmentally sound. The Army has established a goal to reduce its 1985 waste generation levels by 50% by the year 1992. To assist with this goal, the Production Base Modernization Activity (PBMA), under a program sponsored by the U.S. Army Materiel Command (AMC), contracted Science Applications International Corporation (SAIC) in association with Day and Zimmermann, Inc. (D&Z) to conduct a Hazardous Waste Minimization Study (HAZMIN) at six U.S. Army facilities. This study was unique in that it not only addressed hazardous wastes but non-hazardous oily wastes as well (i.e. vehicle crankcase and metal working oils). Presently, only thirteen states classify these petroleum oils as hazardous wastes. Future state regulations, however, could require additional states to designate these wastes as hazardous. This investigation was conducted in three phases to document how hazardous and oily wastes are produced and to recommend waste reduction alternatives.

This paper presents the results of the waste minimization study which was conducted at a U.S. Army Metal Parts Manufacturing Facility, Louisiana Army Ammunition Plant (AAP). Although all waste generating processes were evaluated, including explosive production and plant support activities, this paper will highlight the key waste reduction options recommended for the metal parts manufacturing operations. These processes generate the majority (>90%) of hazardous/non-hazardous wastes plant-wide.

STUDY STRATEGY

The HAZMIN study was conducted in three distinct phases. Phase I quantified the sources and amounts of wastes generated through the development of a hazardous/oily waste generator data base and an on-site hazardous/oily waste treatment data base. Data collected included raw materials, description of the waste generating process, and waste stream volumes. Figures 1 and 2 present examples of these two data bases. Site visits were conducted over a 2 week period to collect this information. Data collection efforts consisted of reviewing available waste generation documents (i.e. internal waste tracking forms and RCRA Part B permit applications) and performing building inspections.

Phase II activities focused on a more detailed examination of each hazardous/oily waste generation process and on-site waste treatment facility. While Phase I activities provided a general understanding of the sources and amounts of waste generated, information gathered during Phase II provided a

Bldg. #	Raw Material	Process Description	Type Waste	Volume per year
1	1,1,1-Trichloroethane	Vapor Degreasing	Spent F002 Solvent	1,000 Gallons
2	Machine Coolant	Machining	Spent Coolant	22,000 Gallons

Figure-1. Phase I Database for Hazardous/Oily Waste Generators

Bldg. #	Waste Treatment Facility	Waste Treated	Volume Treated per year	Contributing Process	Source Building
15	Oily Waste System	Forging Wastewater	2 MG	Forging Washdown	5
16	Heavy Metal System	Metal Finishing Wastewater	3 MG	Rinse Waters/ Bath Dumps	6

Figure-2. Phase I Database for On-Site Hazardous/Oily Waste Treatment Systems

complete technical understanding of how the waste(s) is generated. This information was essential in the development of HAZMIN options. An additional two weeks of visits were conducted to enable the project team to revisit each of these operations. To assist in the collection of information and data, a four page form was developed which was tailored in part after EPA's Waste Minimization Worksheets. The form was a vehicle for collecting and displaying information and data relating to the mechanics and logistics of the operation, the means of waste generation, raw material usage and costs, waste generation and associated disposal costs, material mass balances, and preliminary HAZMIN options. In addition to the process inspections, a "brainstorming" session was held with plant personnel on the final day of the Phase II inspection, to present the project team's preliminary HAZMIN ideas. Through this discussion, feedback received from plant personnel helped to determine the potential feasibility of the ideas and to identify any additional HAZMIN options which the facility desired to investigate.

The Phase I data bases and the Phase II process and facility descriptions served as the basis for the development of the Phase III HAZMIN plan. The HAZMIN plan provided a description of each recommended capital intensive option and general recommendations on a facility wide basis. The feasibility of each HAZMIN option was determined through an in-depth investigation which included contacting equipment vendors, reviewing available literature, and performing economic analyses. In some instances, sampling and laboratory testing was performed to

determine a particular option's viability. Source reduction options were explored first because they were the preferred means of minimizing waste. Where source reduction was not technically or economically practical, recycling techniques were considered followed by on-site treatment options.

FACILITY DESCRIPTION

The Louisiana AAP is a government-owned, contractor operated (GOCO) facility. The contract operator is Thiokol Corporation. In addition to load, assemble and pack operations, the facility manufactures 155 mm projectiles parts which include the bodies, bases, and ogives (removable projectile cone or tip).

There are five primary processes involved with metal parts production: 1) forging, 2) machining, 3) metal finishing, 4) vapor degreasing, and 5) spray painting. These operations result in the generation of approximately 1.5 million kg/yr of hazardous wastes and 1 million kg/yr of non-hazardous oily wastes requiring off-site disposal at an annual cost of \$840,000. Figure 1 provides a breakdown of hazardous/oily wastes generated by amount and disposal cost based on 1989 data. As shown, there are three major waste groups which represent the most significant portion of waste generated: lead contaminated (D008) oily sludge from metal forging operations, spent coolants from machining, and chromium contaminated (D007) sludge from metal finishing operations.

The following is a discussion of the processes generating these wastes and their respective waste reduction options.

METAL FORGING

DESCRIPTION OF OPERATIONS

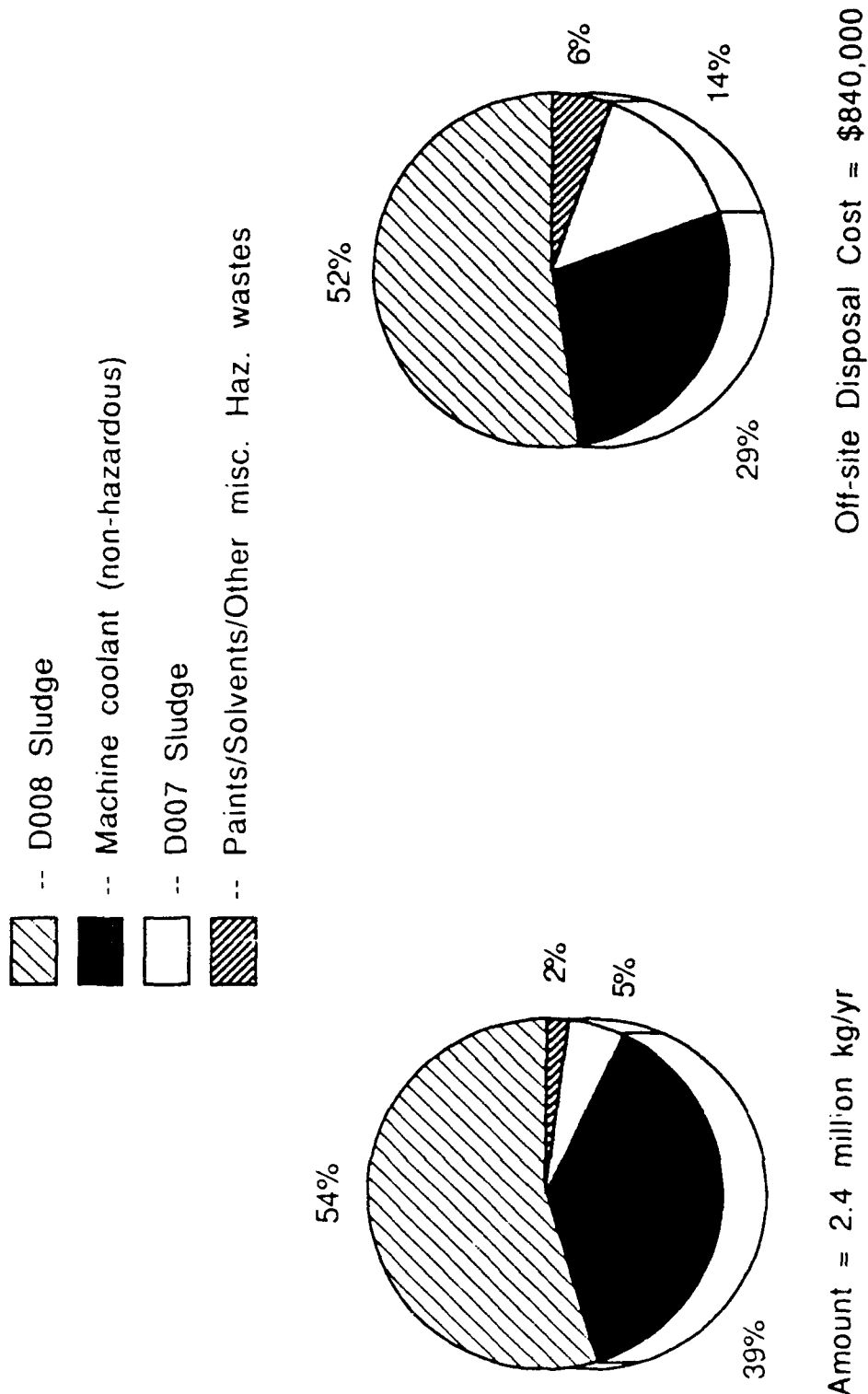
The metal forging process is the initial manufacturing step in the production of 155mm projectile bodies. The process begins with 20 foot long billets of 1340 carbon steel which are then sawed into 12 inch long mults. The mults are heated and then forged. Forging operations occur in three stages to gradually increase the length and transform the mult to the desired shape.

The forging process generates an oily wastewater from end of day washdowns of the forging area. This wastewater is composed of a mixture of waste forging compounds; hydraulic oil, primarily from leakage; and cleaning detergent. The wastewater is treated on-site at the facility's Oily Wastewater Treatment System (OWTS) where approximately two million gallons per year is treated. Treatment of this wastewater produces an oily sludge which for an unknown reason has lead toxicity, resulting in it being transported off-site as a characteristic D008 waste. This sludge is the largest volume of hazardous waste generated at approximately 1.3 million kg/yr, representing approximately 45% of the facility's off-site disposal costs for hazardous and non-hazardous oily wastes.

HAZMIN RECOMMENDATIONS

The HAZMIN strategy for the forging operation examined mechanisms to eliminate the lead toxicity in the sludge and reduce the amount of oily sludge

Figure 3. Breakdown of Waste Generation for Metal Parts Production



generated through a reduction in waste forging compounds and hydraulic oils generated.

With regards to reducing hydraulic oil leakage, plant personnel have already identified major leaks in the forging press area and have recommended an upgrade of the hydraulic system to eliminate gross leakage. This upgrade will include replacement of hydraulic piping, valves, seals, pumps, and other items. As determined by Thiokol, rehabilitation of the hydraulic system will have a capital cost of \$371,000. The projected annual savings is \$525,000 with a payback period of 8.5 months. Projected savings is based on the reduced purchase of hydraulic fluid and reduced treatment and disposal costs. The upgrade, however, is awaiting approval. The project team strongly encouraged the facility to implement this option.

Elimination of the Lead Source in the Oily Wastewater

The oily sludge generated by the OWTS is handled as a D008 characteristic hazardous waste. Plant personnel reported that analyses have consistently shown this waste to be hazardous. It is unclear why this waste exhibits lead toxicity since neither the material forged, nor the forging compound or hydraulic fluids utilized (as supplied by the manufacturer) contain any lead.

The project team conducted sampling during Phase II activities in hopes of identifying the source of the lead and subsequent means for elimination. A number of oily wastes were sampled including the forging compounds and the primary hydraulic fluid. The results of the sampling identified the raw hydraulic fluid to be the source of the lead. A significant concentration of 7mg/kg was detected. This was the second time lead was detected in the raw hydraulic fluid. The facility performed a limited sampling program in 1989 to identify the source of the lead. The results of the sampling were reportedly inconclusive; however, a review of the data also showed the raw hydraulic fluid to contain lead. A similar high concentration was detected. The manufacturer of the hydraulic fluid was contacted. They indicated that lead is not present in the fluid. This was supported by their Material Safety Data Sheet (MSDS).

Based on sampling evidence and manufacturer information, it was evident that the hydraulic fluid was picking up lead prior to its introduction into the forging machinery. Two sources were identified: 1) the delivery tanker itself and 2) the on-site hydraulic fluid storage tanks - leaching of lead could be occurring within the tanks, possibly due to aterne (lead-coated) lining. Follow-up actions were recommended which should serve to isolate the source and eliminate it. This includes analysis of the storage tank lining and collecting a sample of hydraulic fluid directly from the delivery tanker. Dependent upon the result of analyses, actions taken to eliminate the lead, could be recoating or replacement of the storage tanks, or finding a new supplier for hydraulic fluid.

Elimination of the lead will allow the waste to be disposed as a non-hazardous waste. This will result in a hazardous waste reduction of 1.3 million kg/yr and a subsequent disposal cost savings of \$290,000/yr.

Direct Collection of Forging Compound

Waste forging compounds represent most of the "pollutant load" presently sent from the forging area to the OWTS. This is significant since the forging compounds are graphite-based and as such can interfere with the efficient operation of the OWTS. The OWTS is in fact operating poorly with minimal recyclable oil present. Therefore, the direct collection of forging compounds can reduce the volume of oily sludge generated, as well as improve the OWTS treatment efficiency. Additional benefits would also include raw material savings from reuse of collected compound and a reduction in cleanup activity, resulting in reduced labor requirements and cleaning detergent cost.

Two types of graphite based forging compounds are used. Non-water soluble forging compound is applied manually by a brush within the die pots of the presses. Water soluble compound diluted to 50% is automatically applied via ejectors to the press. The forging compound generated as waste is the excess compound which is not flashed off, drippings from brushes used during manual application and overspray (drainage) from the automatic application.

Spilled/excess "raw" compound from manual application was identified as a candidate for collection and reuse. At a brainstorming session with plant personnel during Phase II activities, this idea was discussed and forging personnel noted that they also had considered this option. In fact, they were planning a trial installation of a steel curb around one of the forge presses to collect excess compound and a gutter to direct it back to the compound reservoir (steel bucket) adjacent to the press. Figure 4 depicts the proposed collection system.

Successful implementation of this option will hinge on the ability to reliably drain the viscous compound back to the reservoir. Heat tracing of the line utilizing steam was recommended to keep the compound in a liquid state.

Direct collection was also recommended for waste compound drainage from automatic application. However, this class of forging compound has been subjected to forging conditions and is not acceptable for reuse. Figure 5 illustrates the installation envisioned. The structure would consist of a collection pan around the base of the press and a tank to allow for the direct collection of compound drainage. Additionally, the tank would be equipped with caster and hoist points to facilitate its regular removal from the forge sump for transfer to a larger above ground tank.

It is projected that successful implementation of this option (along with repair of the hydraulic system) will result in a 50-70% reduction in oily sludge volume, assuming collection of 60% of each type of compound. Based on the oily sludge being non-hazardous in the future, annual disposal cost savings (less forging compound disposal cost) is estimated at \$58,000 to \$88,000. Additionally, the direct collection of forging compound is anticipated to result in a 50% reduction in both labor and cleaning detergent chemical costs for steam cleaning activities. Total annual savings, in terms of disposal and raw material (forging compound and detergent) costs, is estimated at \$133,000 to \$163,000.



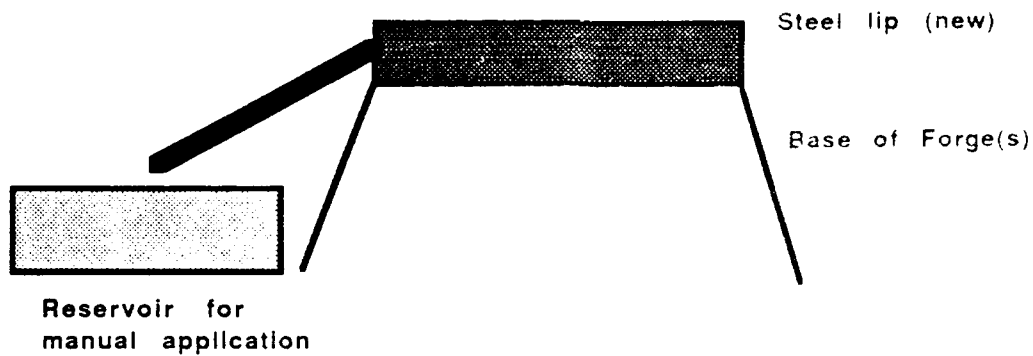


Figure 4
Proposed Collection / Reuse
System for Manually Applied
Forging Compounds

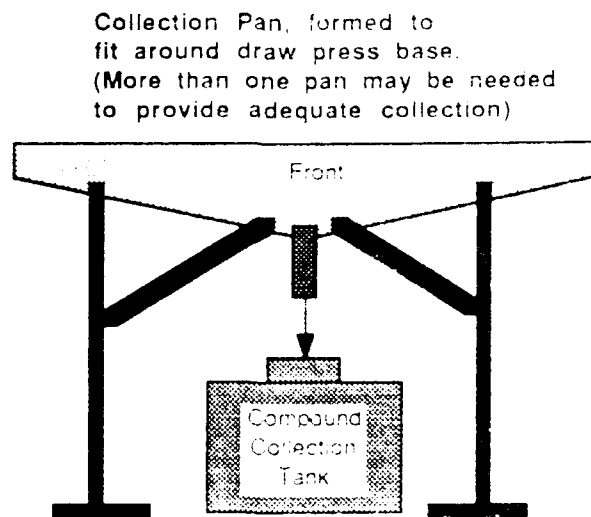


Figure 5
Proposed Collection System for
Automatically Applied Compounds

MACHINING

DESCRIPTION OF OPERATIONS

The machining of metal ammunition parts (projectile bodies, ogives, and bases) is conducted in two areas within the facility. The largest operation is involved with the production of 155mm projectile bodies.

Spent soluble oil machine coolant is the major waste generated from machining operations. During 1989, approximately 245,000 gallons were disposed, representing the second largest volume of waste generated. The disposal cost for this waste is \$.98/gallon. Waste hydraulic and other machine oils are also generated in a much lesser amount and are recycled off-site at a nominal transportation cost of \$300/yr. Therefore, machine coolants were the major focus of waste reduction.

Machine coolants are used to reduce the effects of friction from machining operations. Machine coolants used at the facility are diluted to a 5% concentration with water. The coolant is either stored in a reservoir within the individual machines or a central reservoir serving several machines. A central reservoir serves the majority of machines employed with projectile body manufacturing. A large scale 20,000 gpd coolant filter recycle system is employed for this central reservoir. Smaller 5000 gpd disposable media filter systems are utilized for other machines. Even with the use of filter systems the periodic replacement of coolant is necessary due to degradation, primarily the result of tramp oil and bacterial contamination. The main coolant system is changed out three to four times per year, representing the largest source of spent coolant (>75%). In addition to the coolant degradation, waste coolant is also generated from coolant dragout collection from scrap metal turnings (shavings). Scrap metal collected by the machines is placed in outdoor dumpsters which are located on curbed drainage pads. Drainage for the dumpsters is collected and disposed with other waste coolant.

HAZMIN RECOMMENDATIONS

HAZMIN options were aimed at extending the useful life of the coolant, to reduce the volume of waste coolant generated. Recognizing, however, that coolant would still require disposal, treatment options were also investigated to reduce the volume of coolant disposed.

The facility has already instituted a number of useful procedures to extend the life span of the coolant, including weekly testing of coolant for pH, tramp oil, total oil and percentage coolant, and logging individual machine oil usage to identify repairable leaks.

Improved Housekeeping

Scrap shavings from machining operations served by the main coolant system are conveyed by a "harpoon" system. This transport mechanism segregates coolant to the coolant filtering system while shavings are conveyed to outside rail cars. Conversations with plant personnel and direct observation lead the project team to conclude that the main coolant recycle/scrap transport system is prone



to accumulate chips and other solid matter in numerous sumps and channels. Dirt and chip accumulation can retain tramp oil and can provide sites for bacterial growth which may be contributing to the a shortened coolant life span.

To aid in extending coolant life, a regular program of cleaning the transport system was recommended. Cleaning activities will include periodic drainage of either portions of, or the entire transport channel followed by manual removal of the accumulated materials. It is not possible to forecast the magnitude of the effect the program would have on the life of the coolant. However, since coolant disposal and raw material costs for this area are approximately \$340,000, significant benefits could be realized.

Use of High Quality Water For Coolant Makeup

The quality of water used for dilution of machine coolants is a critical factor in the success of the coolant. The useful life of the coolant product quality and raw material usage are all affected by the quality of water utilized. The total dissolved solids (TDS) concentration of the makeup water is of particular concern. Waters with greater than 100 ppm TDS can adversely affect the coolant, as well as the items machined. Sulfates and chlorides at 100 ppm contribute to corrosion problems. Sulfates also enhance bacterial growth, as they are biochemically reduced to hydrogen sulfide creating a rotten egg odor.

Analytical data on the facility's water supply wells was reviewed. This water is used for the makeup of machine coolants. The data revealed TDS levels well above 100 mg/l. Most notably was the TDS concentration of 813 mg/l reported for wells which supply water to the main machining area, including the machines served by the main coolant filter system.

Based on the analytical data, it was recommended that high quality (deionized or reverse osmosis treated) water be considered for initial makeup of the coolant. Since coolant is disposed on an infrequent basis, an economic alternative to installation of a permanent system is the use of a portable trailer mounted system. This service is provided by a number of water treatment firms and can be leased or rented.

It was recommended that the facility try this service on a trial rental basis in the main coolant system to determine its actual benefits. The service would be utilized each time a new coolant batch is made up, which is presently three to four times per year. If the use of high quality water helps to extend coolant life, this service should be permanently used. Based on the facility's needs, the cost of the service is approximately \$2500 per rental. The annual cost savings cannot be determined at this time as the impact is not known. However, for the purpose of estimating potential savings, if this option is successful in reducing the need for coolant change-out by 50%, the resultant estimated annual raw material and disposal cost savings would be approximately \$38,000.

Emulsion Breaking of Waste Coolant

Machine coolants utilized at the facility are soluble oil fluids which are made up with one part coolant and 20 parts water. An attractive method to reduce the volume of coolant disposed is to separate the oil and water through emulsion breaking. The objective of the emulsion breaking is to recover the oil fraction

for off-site disposal and discharge the remaining aqueous phase to the plants sanitary sewer system. Sewering of the aqueous phase, following emulsion breaking, is an acceptable disposal option recommended by the coolant manufacturer, as stated in the MSDS.

Two technologies with potential applications in breaking coolant emulsions were identified. They are 1) ultrafiltration and 2) pH adjustment followed by quiescent separation. Although both of these technologies could be successful, low capital costs and relatively unsophisticated operational requirements make the second option preferable.

In this process, the pH of the waste coolant is dropped to between 2-4 to split the emulsion. The waste is allowed to stand for a period of time (hours to several days) resulting in a floating oil layer. This layer can then be decanted to a spare holding tank for off-site disposal. The clear layer is raised to approximately pH 7 and then slowly bled into the sanitary sewer.

Depending on the effectiveness of the emulsion break, the reduction of coolant volume is projected at 60-95%. The capital cost is approximately 95,000 with a projected net annual savings (savings less operating costs) range of \$75,000 to \$125,000. Additional savings could also be realized if the oil layer can be disposed as a recyclable oil.

To support our contention that this option was viable, an informal treatability screening was performed on the primary coolant used. Results of the tests were encouraging. An effective split formed over a 24 to 48 hour period. Additionally, analyses were conducted on the aqueous phase for oil and grease and chemical oxygen demand, to determine the potential impact to the sanitary system. These results showed that the facility is capable of handling this additional pollutant load. This was substantiated by an inspection of the sanitary plant and a review of discharge data.

Covering Outdoor Sumps

As discussed, a portion of waste coolant generated, approximately 15%, is coolant dragout collected in outdoor sumps. Since the sump is not covered, a significant portion of the coolant collected is rainwater. Plant personnel estimated as much as 90% of the coolant disposed (37,000 gallons per year) can be accounted for as rainwater. This is substantiated by annual rainfall figures and dimensions of the drainage pad. As a simple means to resolve this problem, it was recommended that an open sided roofed structure over the sump be constructed. Depending on the material utilized the capital cost can range from \$35,000 to \$45,000. Assuming a 90% reduction in the volume of coolant disposed from this area, the off-site disposal cost savings would be approximately \$33,000. Disposal cost saving with the emulsion breaking process, assuming a 60% to 95% volume reduction, would be \$1600 to \$13,000. Covering the sumps will also serve to reduce treatment chemical and labor costs incurred by the emulsion breaking process.

METAL FINISHING

DESCRIPTION OF OPERATIONS

Metal Finishing operations consist of alkaline cleaning, paint stripping, phosphatizing, and chrome etching. The metal finishing process generates wastewaters from discharge of rinse waters and batch dumping of process tanks. Wastewaters are treated on site and their treatment results in the generation of chromium contaminated (D007) sludge. Based on material balance on the metal finishing process, the primary source of chrome is from the etch process. Chrome contribution from batch dumping of chromate seal tanks in the phosphatizing line is considered to be insignificant in terms of chromium toxicity.

HAZMIN RECOMMENDATIONS

HAZMIN options focused on reducing or possibly eliminating the generation of chromium contaminated sludge through emphasis on the chrome etch process. If this was not feasible, treatment options were considered to reduce the volume of waste generated

Electrodialytic (ED) Process for Chrome Etching Operation

A major renovation of the metal finishing area is planned which could have a significant impact on chromium sludge generation. The renovation will include a non-chrome (ammonia-based) etch process. The status of the project is presently uncertain. As an alternative to the non-chrome etch process, an electrodialytic (ED) process, to recover and recycle the chrome, was recommended. The project team recognized that the non-chrome etch process is a much preferred option, as it would totally eliminate the use of the chrome.

The ED process converts trivalent chromium to reusable hexavalent chromium and also serves to remove any metal impurities, such as copper and zinc. These metals are removed as a hydroxide sludge. The process can be operated in a closed loop system. The rinse waters would be collected and returned to the enchant as makeup water. Figure 6 illustrates the ED process while figure 7 depicts the closed-loop system.

The capital cost for this option is \$21,750 which includes an installed equipment cost of \$15,000. The projected net annual savings is \$95,000. With the implementation of the ED unit, all sludge generated at the treatment facility is anticipated to be non-hazardous, resulting in a hazardous waste reduction of approximately 120,000 kg/yr. Additional disposals cost savings could be realized if the hydroxide sludge could be sold to a waste exchange service for its metal content. In addition to disposal savings, raw material purchases are projected to be reduced by 90%.

An ion exchange unit was also considered for the chromate seal baths however, it was not recommended at this time because the chrome toxicity from the seal tanks is believed to be insignificant. Additionally, phosphoric acid refortification of the baths was recommended to extend bath life. However, an ion exchange unit was recommended for future consideration if chrome toxicity still exists after implementation of the ED process.

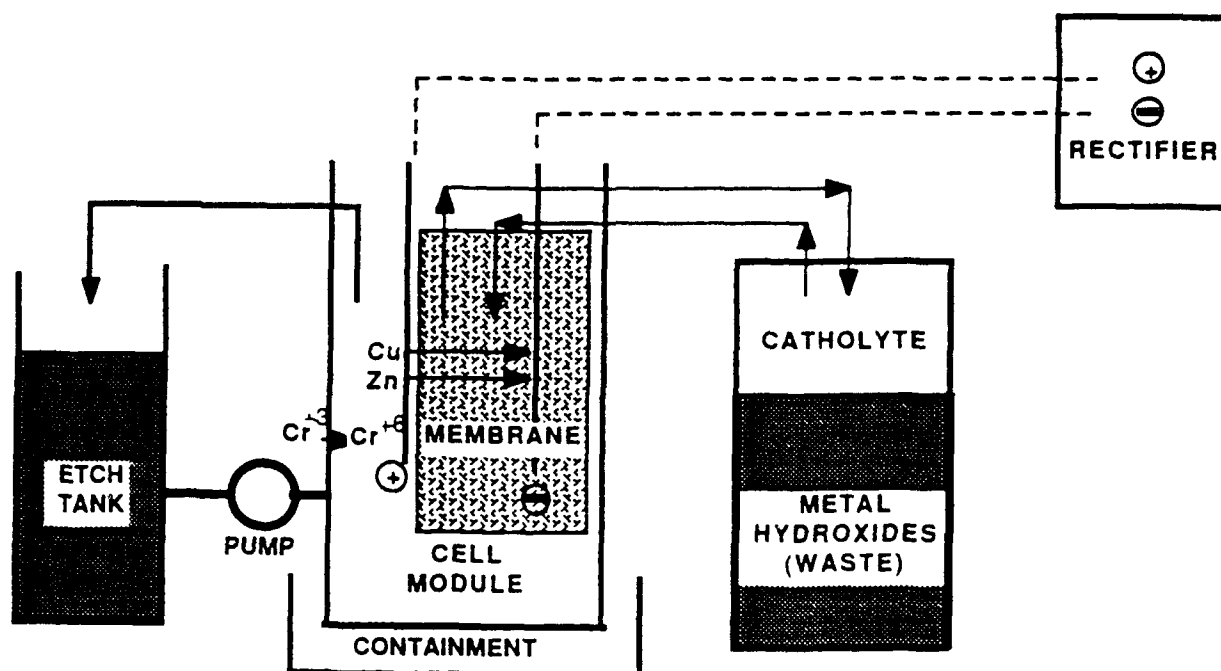


Figure 6. Electrodelectrolytic (ED) System for Chrome Etching Process

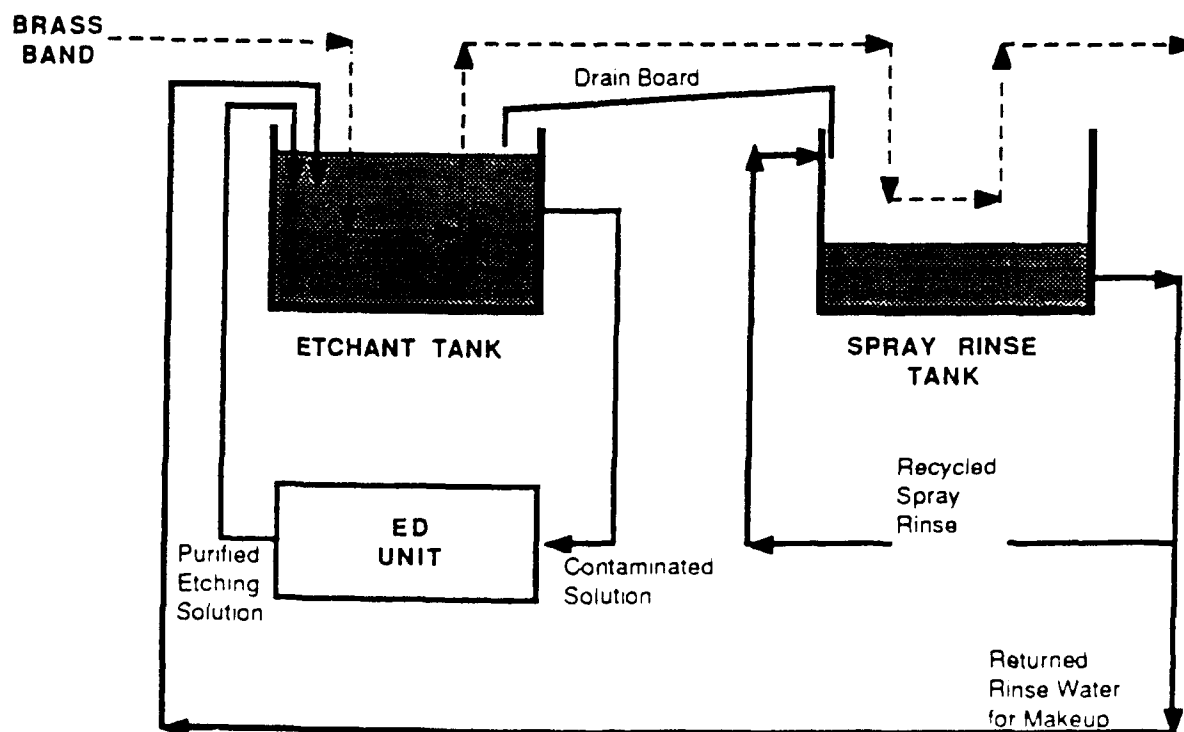


Figure 7. Close-loop Etching System

Treatment Options

Treatment options were also considered to reduce the volume of sludge generated. A viable option was to first segregate the chrome bearing sludges from the non-chrome bearing sludges prior to dewatering in the filter press and then to use a sludge dryer to provide further volume reduction of the contaminated sludges. Although chromium contaminated wastestreams contribute only 5% of the total sludge volume, all sludge is rendered hazardous due to the combined processing of the sludges. This option was not recommended since the chromium recovery options are expected to eliminate the generation of hazardous sludge.

Although all sludge is anticipated to be non-hazardous, pH optimization of the plant was recommended to possibly reduce sludge volumes and improve dewatering characteristics. This will be beneficial to improve treatment efficiency and reduce treatment costs. Optimization steps included conducting jar tests to determine the appropriate chemical and doses for sludge thickening.

SUMMARY

A three phase HAZMIN study was conducted at a U.S. Army Metal Parts manufacturing facility. This paper highlighted some of the key options recommended for the metal parts manufacturing processes. These options will have the most significant impact on hazardous/oily waste generation as they affect the three major waste groups, in terms of volume generated and disposal cost. Facility-wide, thirty six waste minimization options were recommended for implementation at the facility. These options, if successfully implemented, have the potential to reduce hazardous waste generation by 90% and non-hazardous oily waste generation by 60-95%. The capital cost for these options is estimated at approximately \$210,000. The net annual savings (savings less operating costs) is projected to be \$730,000.

In addition to process specific options, a number of general facility wide options were recommended and included a management initiative program where facility personnel are financially rewarded for successfully implemented HAZMIN options and a employee education program to increase employee awareness of the importance of waste reduction activities.

Overall plant personnel were found to be very conscious of keeping waste generation to a minimal level. The facility has implemented and is investigating a number of HAZMIN options. In addition to options discussed, plant-initiated options include a procedural change to eliminate the need for vapor degreasing on certain parts and evaluation of a powder spray paint technology to replace solvent-based spray painting methods.

Cooperation from facility personnel was excellent and was key to the successful completion of this study. Additionally, this study was greatly aided by the plant's effective waste tracking procedures, material record keeping, and personnel knowledge of operations.

In conclusion, the methods and strategies used to conduct this study can be successfully employed for developing a pollution prevention program at any type of facility. A number of useful tools can be used to generate waste



reduction options, including a review of waste generation data, process evaluations, literature investigations, and contacting equipment vendors. In addition, as demonstrated by this study, conducting sampling activities and laboratory studies can be an integral part in identifying ways to reduce waste.

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THE IVADIZER (ALUMINUM ION VAPOR DEPOSITION SYSTEM)
AS A REPLACEMENT FOR CADMIUM ELECTROPLATING
AT U.S. ARMY INSTALLATIONS

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INTRODUCTION

USATHAMA conducts R&D projects to minimize hazardous waste generation at Army depots. One such project was to install an Aluminum Ion Vapor Deposition System or Ivadizer at the Anniston, Alabama Army Depot. The idea was to replace cadmium electroplating with aluminum coatings.

Cadmium electroplating provides a corrosion resistant finish on metal surfaces. However, cadmium is toxic and carcinogenic. Additionally, cadmium plating baths contain cyanides. Treating the rinse water and spent plating solutions generates hazardous wastes. Aluminum coating does not generate hazardous wastes. Therefore, replacing cadmium with aluminum plating would reduce the amount of hazardous wastes generated at an Army depot.

The Ivadizer operates by depositing positively charged aluminum ions onto a negatively charged metal surface. In this sense, it is similar to cadmium electroplating.

Ivadizer operations are started by pumping the chamber (see Figure 1) down to a maximum pressure of 9×10^{-5} Torr. Argon gas is introduced into the chamber to raise the pressure to about six microns. Through a high voltage discharge, some of the argon is ionized. The positive ions bombard the metal surface and provide final cleaning. Pure aluminum wire is fed into ceramic boats which are heated by electrical resistance. The wire is melted and then vaporized. The aluminum vapor is ionized by contacting the argon ions. The aluminum ions are attracted to the metal surface and are deposited as a thin metal film. The boats move up and down the chamber at a controlled speed. The boat speed determines the thickness of the coating because the slower the boats move up and down the chamber, the more aluminum is vaporized and the thicker the coating. Larger parts are hung from an electrically insulated plating rack (see Figure 2). Nuts, bolts, and small parts are put inside a rotating cylinder that has an open mesh structure (barrel coater -- see Figure 3).

COATING CLASSES

The specifications for aluminum and cadmium coatings use the same terminology of Classes 1, 2, and 3 and Types I and II. The classes define the respective coating thickness with Class 1 being the thickest and Class 3 being the thinnest. Type I is an as-is coating and Type II receives a subsequent chromate conversion coating. The coating procedures for Types I and II aluminum coatings are identical and applying the chromate conversion coating to Ivadized aluminum presented no problems. Table 1 presents the coating thickness specifications for aluminum and cadmium coatings.

Classes 1, 2, and 3 cadmium and aluminum coatings are not comparable. Taking into account the densities and atomic weights of the metals, for the same thickness coating, aluminum would provide 30 percent more protection on a gram atomic weight basis, for the same thickness as Cd. This is because there are more atoms of aluminum than cadmium available to provide corrosion



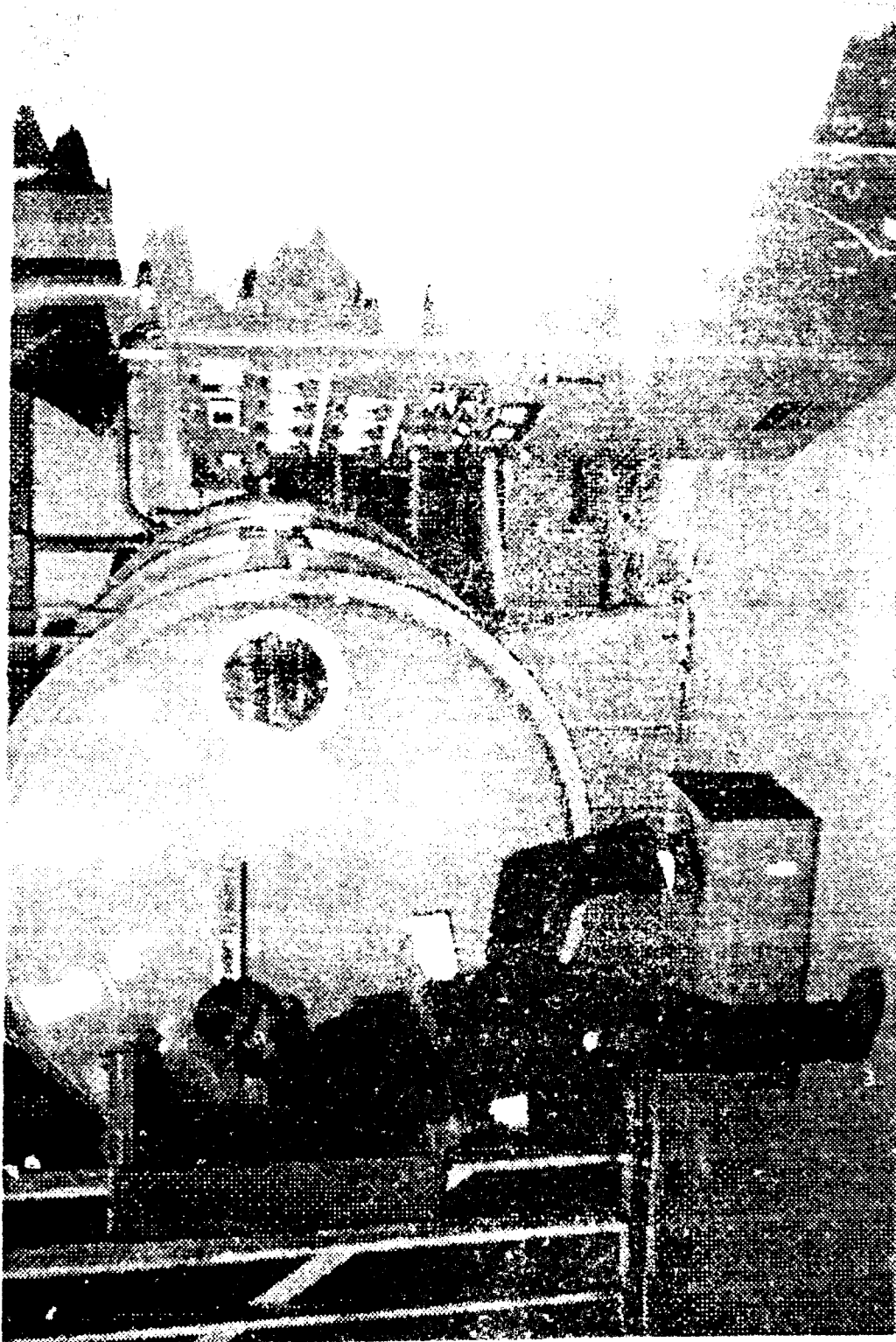


Figure 1. An Iyadizer and control panel.

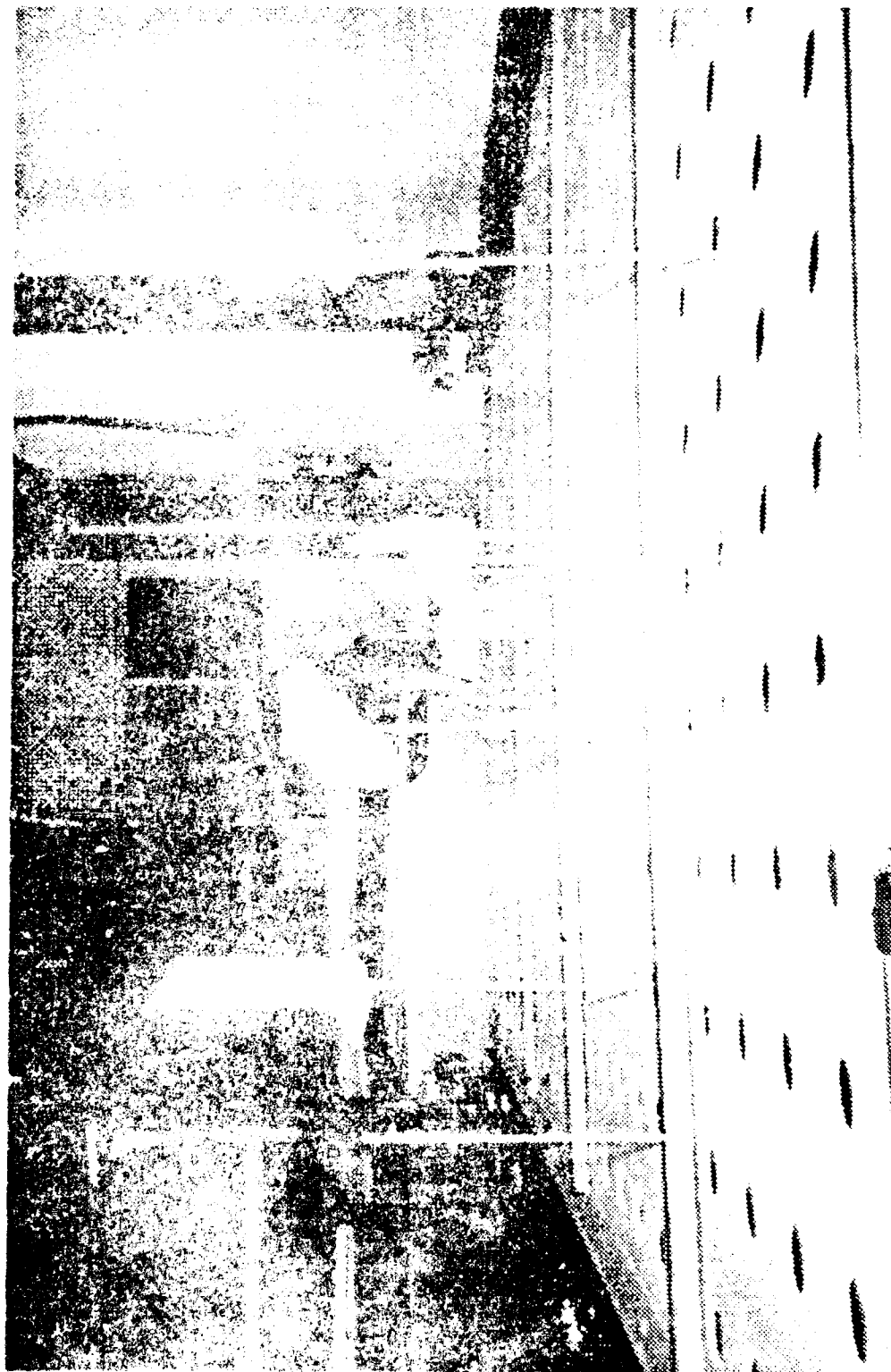


Figure 2. Plating rack with parts suspended from
the rack by wire hooks.

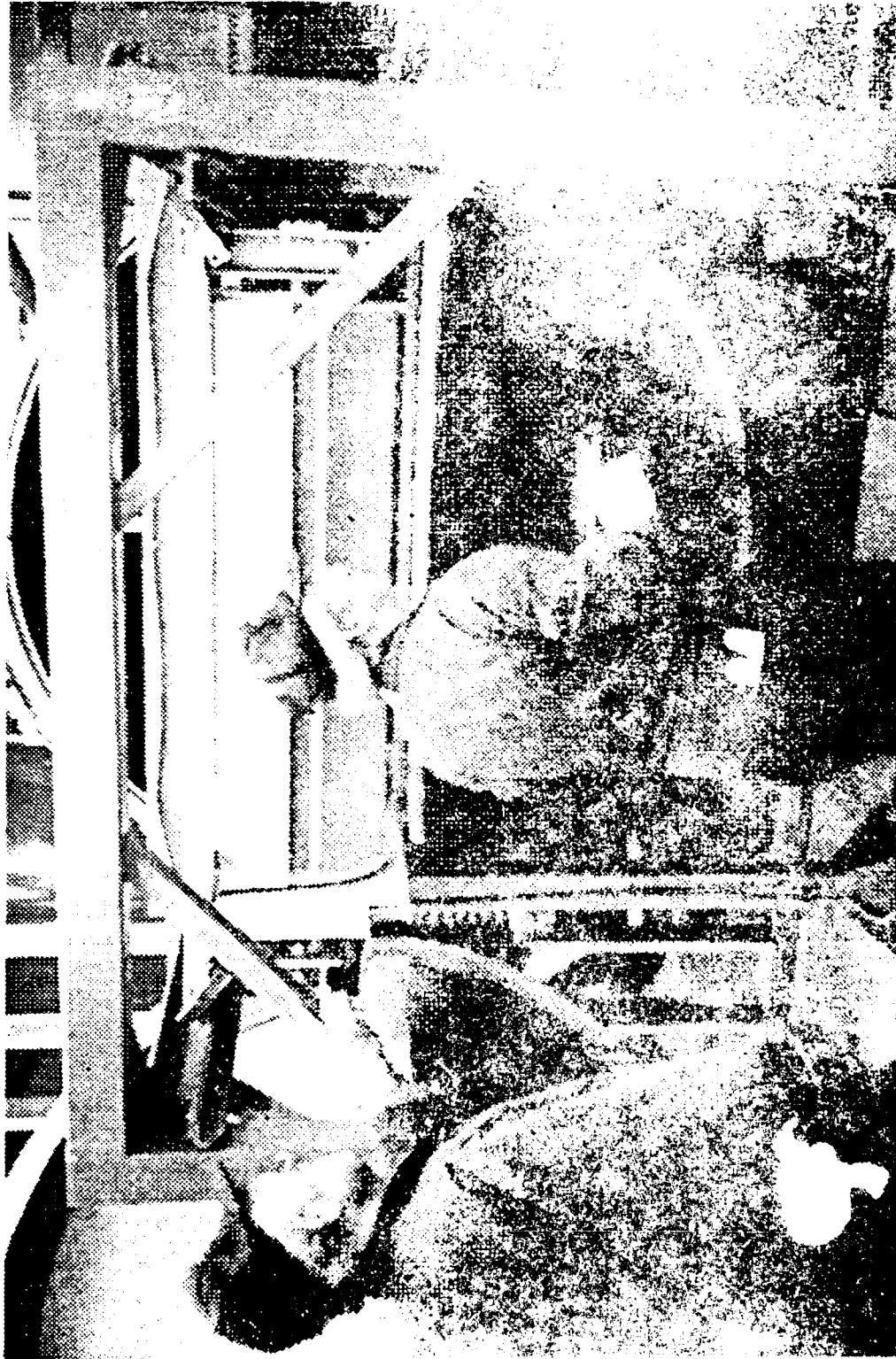


Figure 3. Loader with the chamber door open and a rotating barrel coater in place.

**TABLE 1. SUMMARY OF MINIMUM COATING THICKNESS
REQUIREMENTS FOR CADMIUM ELECTROPLATES
AND VAPOR DEPOSITED ALUMINUM**

Class	Coating Thickness (mils)		
	Cadmium		Aluminum
	Area touched by 0.75" ball	Area not touched by 0.75" ball	
1	0.50	0.30	1.00
2	0.30	0.20	0.50
3	0.20	0.15	0.30

protection. Table 2 shows salt spray test requirements and that a Class 3 aluminum coating provides equal or superior protection than a Class 1 cadmium coating.

**TABLE 2. CORROSION RESISTANCE REQUIREMENTS
OF CADMIUM AND ALUMINUM COATINGS**

Class	Hours in salt spray booth			
	Cadmium		Aluminum	
	w/o conver- sion coating	with conver- sion coating	w/o conver- sion coating	with conver- sion coating
1	96	168	504	672
2	96	168	336	504
3	96	168	168	336

Besides the advantage of better corrosion protection, aluminum coatings have better adherence to the base metal, a higher maximum service temperature (950°F versus 450°F for Cd), and no potential for hydrogen embrittlement.

On a special handling basis, cadmium electroplates can coat inside a cavity such as a pipe by extending an anode into the

cavity (not normal procedure). The Ivadizer can coat one diameter inside a cavity. Thus, the Ivadizer cannot meet the equivalent class coating for deep cavities (greater than one diameter) without using another coating such as epoxy paint.

TORQUE REQUIREMENTS

Aluminum coated threaded fasteners such as nut and bolt combinations require more torque to make a threaded connection than do cadmium coated fasteners. This is because aluminum has a higher coefficient of friction. Data from the McDonnell-Douglas report⁽¹⁾ indicate that the average difference is significant (about 25 percent). The McDonnell-Douglas report provides data that show that torqueing requirements established for cadmium plated fasteners can be used for aluminum plated fasteners if the aluminum is lubricated (molybdenum disulfide and cetyl alcohol have been used) or if one member of the fastener combination is cadmium plated (usually the nut). Alternatively, different-and-higher torqueing requirements could be established for aluminum coated fasteners.

IVADIZER TESTS

There are about 70 Ivadizers in successful commercial operation. Most of the applications have been on Navy, Air Force, and commercial aircraft. The Anniston test program had the objective to determine to what extent the Ivadizer could replace cadmium plating at Army depots.

Eighty-six (86) parts used on Army vehicles and engines that could be identified by combinations of part number, shape, and/or function, were successfully aluminum plated in the Ivadizer. Additionally, nuts, bolts, brackets, and other small parts were successfully aluminum plated in a barrel coater. On the very few occasions when coatings had thin areas that did not meet coating thickness specifications, these specifications were subsequently met by changing operating conditions such as how the part was



positioned on the plating rack, plating for longer periods, and plating in two stages with the part being rotated after the first stage.

Because of part availability, both scrap and production parts were processed. After processing production parts, the aluminum coatings were removed and the parts returned for normal use.

Test results were summarized on a summary sheet (Table 3). Information presented is:

- ° Part number (if available)
- ° Part description (if available)
- ° Vehicle or engine where part is used
- ° Test results data - test date, class of coating, pass (P) or fail (F) testing, type of testing (V = visual, T = thickness, CC = chromate conversion, SS = salt spray). Thickness measurements were made on every type of part processed in a run. Coating thickness measurements were made on every part if five or less of that type were run. If more than five parts, measurements were made on at least half of the parts. Particular attention was given to thickness measurements near recessed areas, bends, and cavities.

Data for individual runs were kept on a Run Data Sheet (Figure 4). The information on the first page of the Run Data Sheet (I. Run Summary) shows that this run was the first of the day on March 11, 1991, and was a Class 3, Type II coating (the most common). The wire feed rate was 35 percent of the maximum possible wire feed rate. This was the manufacturer's recommendation.

During this run, the boats holding the molten aluminum made two passes up and down the plating chamber. The first pass at 100 percent boat speed and provided the required thin coating necessary for good adhesion. The second, slower run was at 70 percent boat speed and provided the necessary aluminum thickness.

TABLE 3. PRODUCTION PARTS PROCESSED IN THE IVADIZER

Part No. (if available)	Part description (if available)	Vehicle or engine where part is used	1st Test	2nd Test	3rd Test	4th Test	5th Test	6th Test	7th Test	Comments
739890			3/13, 2 P (V, T)							
7404673	Spring, drivers seat compression	M60	3/1, 2 P (V, T)							
7973841	Gasket	1790 Eng	2/5, 3 P (V, T)							
W830010			2/19, 3 P (V, T)							
8619454	Mount, machined	M60	1/29, 3 P (V, T, CC)							
8619488	Support	M60	1/28, 3 P (V, T, CC)							
8725184	Retainer, crankshaft packing	1790 Eng	1/28, 3 P (V, T)	1/30, 3 P (V, T)	2/19, 3 P (V, T)	2/27, 3 P (V, T)	2/27, 3 P (V, T)			
8761080	Eye, engine lifting	M60	3/11, 3 P (V, T)							
8761083	Connector, cylinder head drain tube	M60	1/30, 3 P (V, T)							
8761088	Curved steel drain pipe	M60	3/11, 3 P (V, T)							
8761110	Neck, oil filter & indicator tube	M60	2/19, 3 P (V, T)							
8761111	Gas cap level	M60	11/28, 2 P (V, T)	12/15, 2 P (V, T) f (T)	1/24, 2 P (V, T)	1/29, 3 P (V, T)	1/30, 3 P (V, T)			Positioning? 12/15, non-uniform coating with thin areas
8761136	Flange, intake manifold	1790 Eng	2/5, 3 P (V, T)	2/19, 3 P (V, T, CC)	1/24, 2 P (V, T)	3/5, 3 P (V, T)				

(continued)

TABLE 3. (continued)

Part No. (if available)	Part description (if available)	Vehicle or engine where part is used	1st Test	2nd Test	3rd Test	4th Test	5th Test	6th Test	7th Test	Comments
8781187		M60	1/29, 3 P (V, T)							
10527981	Threaded pin		3/11, 3 P (V, T)	3/12, 3 P (V, T, cc)						
10865824	Engine bolt	M60	3/14, 3 P (V, T)							
10865283	Flange, intercylinder camshaft screen	1790 Eng	1/28, 3 P (V, T)	2/5, 3 P (V, T)	2/19, 3 P (V, T)	2/27, 3 P (V, T)	3/11, 3 P (V, T)	3/12, 3 P (V, T)	3/13, 2 P (V, T)	
10865316	Angle bracket	1790 Eng	11/28, 3 P (V, T)	2/24, 2 P (V, T)	1/28, 3 P (V, T)	1/28, 3 P (V, T)	2/19, 3 P (V, T)	2/27, 3 P (V, T, cc)	2/27, 3 P (V, T)	Passed 4 other tests
10865331	Support, fuel injection line	1790 Eng	2/5, 3 P (V, T)	2/27, 3 P (V, T)	2/27, 3 P (V, T)	2/28, 3 P (V, T)	3/5, 3 P (V, T)			
10865332	Support, fuel injection line clamp	1790 Eng	1/31, 3 P (V, T)							
10865334	Support, fuel injection line clamp	1790 Eng	2/27, 3 P (V, T)	3/12, 3 P (V, T)	3/13, 3 P (V, T)					
10865335	Support, fuel injection line clamp	1790 Eng	11/27, 3 P (V, T)	2/20, 3 P (V, T)						
10865375	Bracket, angle	1790 Eng	12/10, 3 P (V, T)	12/12, 2 P (V, T, ss)	2/5, 3 P (V, T)	2/13, 2 P (V, T)	2/19, 3 P (V, T)	2/28, 3 P (V, T)	3/5, 3 P (V, T)	Passed 2 other tests
10871206	Wedge, prism lock	M60	1/15, 2 P (V, T)	1/23, 2 P (V, T)	1/28, 3 P (V, T)	2/27, 3 P (V, T)				1/23 Thin in recessed area, equivalent to cadmium plating
10873682			3/11, 3 P (V, T)							
10882773			3/11, 3 P (V, T)							

(continued)

TABLE 3. (continued)

Part No. (if available)	Part description (if available)	Vehicle or engine where part is used	1st Test	2nd Test	3rd Test	4th Test	5th Test	6th Test	7th Test	Comments
10915240	Pedal, brake	M60	1/30, 3 P (V, T)	2/14, 3 P (V, T)	2/19, 3 P (V, T)	2/27, 3 P (V, T)	3/13, 3 P (V, T)			
10935478	Spacer, sleeve	1790 Eng	2/27, 3 P (V, T)	2/27, 3 P (V, T)	2/28, 3 P (V, T)	2/28, 3 P (V)				
10935619	Neck, oil filter & gauge rod tubes	1790 Eng	1/15, 2 P (V, T)	1/29, 3 P (V, T)	3/5, 3 P (V, T)	2/4, 3 P (V, T)	2/28, 3 P (V, T)			1/15 thincasting in side neck, equivalent to cadmium plate
10941008	Tube, slotted guide, storage rack	M60	1/30, 3 P (V, T)	2/19, 3 P (V, T, cc)	2/27, 3 P (V, T, cc)	3/5, 3 P (V, T)	3/13, 3 P (V, T)			
10941018	Handle assembly	M60	2/5, 3 P (V, T)	2/28, 3 P (V, T)	3/5, 3 P (V, T)					
10948338	Housing for torsion bar	M551	2/23, 3 P (V, T, cc)							
10918349	Key, torque recoil guard	M551	3/1, 2 P (V, T)							
10948398	Torsion bar housing	M60	3/5, 3 P (V, T)							
10948664	Torsion bar	M551	2/4, 3 P (V, T)	2/5, 3 P (V, T)	2/19, 3 P (V, T)	2/27, 3 P (V, T)	2/27, 3 P (V, T)	3/12, 2 P (V, T)		
10953993	Spring, helical torsion	M60	3/1, 2 P (V, T)	3/5, 3 P (V, T)						
10955921	Lever, door cupola	M551	2/5, 3 P (V, T, cc)	3/11, 3 P (V, T)						
10955925	Lever lock, door handle	M551	2/5, 3 P (V, T)							
11591586	Screen, air intake	M551	2/1, 3 P (V, T)	2/19, 3 P (V, T)	2/27, 3 P (V, T)					

(continued)

TABLE 3. (CONTINUED)

Part No. (if available)	Part description (if available)	Vehicle or engine where part is used	1st Test	2nd Test	3rd Test	4th Test	5th Test	6th Test	7th Test	Comments
11636383	Ring, part of grenade launcher	M551	3/1, 2 P (V, T)	3/13, 2 P (V, T)	3/15, 2 P (V, T)					
11636384	Ring, part of grenade launcher	M551	3/1, 2 P (V, T)	3/13, 2 P (V, T)	3/15, 2 P (V, T)					
11643674	Tube, grenade launcher	M551	3/1, 2 P (V, T)	3/13, 2 P (V, T)	3/15, 2 P (V, T)					Good coating in all but 2" of tube
11664963	Tube assembly, grenade launcher	M551	3/1, 2 P (V, T)	3/13, 2 P (V, T)	3/15, 2 P (V, T)					
11655057	Wedge, vision block retainer	1790 Eng	1/29, 3 P (V, T)	1/30, 3 P (V, T)	2/19, 3 P (V, T)	2/27, 3 P (V, T)	3/13, 2 P (V, T)			
11682768	Bracket, cooling fan support	1790 Eng	11/28, 2 P (V, T, cc)	1/30, 3 P (V, T)	2/5, 3 P (V, T)	2/13, 3 P (V, T)	2/19, 3 P (V, T)	2/28, 3 P (V, T)	3/11, 3 P (V, T)	Two other runs
11683952	Connector, male	1790 Eng	12/4, 3 P (V, T, cc)	12/15, 2 P (V, T), F (ss)	1/30, 3 P (V, T, cc)	2/19, 3 P (V, T)				This part has a cavity at a 45° angle and requires careful positioning
11683970	Eye, engine lifting	1790 Eng	1/28, 3 P (V, T)	1/30, 3 P (V, T)						
11684019	Plate, mounting, fuel-water separator	1790 Eng	2/19, 3 P (V, T)	2/27, 3 P (V, T)	3/11, 3 P (V, T)	3/12, 3 P (V, T)				
11684020	Bracket, throttle control	1790 Eng	2/4, 3 P (V, T)	2/19, 3 P (V, T)	2/27, 3 P (V, T)					
11684128	Bracke, angle	1790 Eng	1/22, 3 P (V, T)	1/29, 3 P (V, T)	2/29, 3 P (V, T)	2/28, 3 P (V, T)	1/22 coating was thin in a recessed area			
11684147		1790 Eng	3/12, 3 P (V, T)							
11684155		1790 Eng	3/12, 3 P (V, T)							

(continued)

TABLE 3. (continued)

Part No. (if available)	Part description (if available)	Vehicle or engine where part is used	1st Test	2nd Test	3rd Test	4th Test	5th Test	6th Test	7th Test	Comments
11684160	Support, fuel injection line	1790 Eng	1/28, 3 P (V, T)	1/31, 3 P (V, T)	2/5, 3 P (V, T)	2/19, 3 P (V, T, cc)	3/11, 3 P (V, T)	3/12, 3 P (V, T)		
11684234	Bracket, cooling fan shroud	1790 Eng	1/24, 2 P (V, T)	1/28, 3 P (V, T)	3/11, 3 P (V, T)	3/12, 3 P (V, T)				
12251905	Strap, blower motor	M60	1/17, 2 P (V, T)	1/22, 2 P (V, T)	1/23, 3 P (V, T)	1/28, 3 P (V, T)	1/29, 3 P (V, T)	2/19, 3 P (V, T)	Pass 3 other tests. Jan 22 problem may be due to cleaning	
12254292	Bracket, cooling fan support	1790 Eng	1/24, 2 P (V, T)	3/5, 3 P (V, T)						
12254297	Spacer	1790 Eng	2/27, 3 P (V, T)	3/11, 3 P (V, T)	3/12, 3 P (V, T)					
12273826	Clamp	M1	2/5, 3 P (V, T)	2/19, 3 P (V, T, cc)						
12273827	Clamp	M1	3/12, 3 P (V, T)							
12274702	Link	M60	2/5, 3 P (V, T)							
12275001	Hook with eye	M60	1/30, 3 P (V, T)	2/4, 3 P (V, T)	2/19, 3 P (V, T)	2/27, 3 P (V, T)	2/27, 3 P (V, T)	2/28, 3 P (V, T)	3/5, 3 P (V, T)	
12275712	Bracket, solenoid	1790 Eng	1/24, 2 P (V, T)	1/28, 3 P (V, T)	1/30 P (V, T)	2/4, 3 P (V, T)	2/28, 3 P (V, T)	3/5, 3 P (V, T)	3/11, 3 P (V, T)	
12283742	Level	M60	3/11, 3 P (V, T)	3/12, 3 P (V, T)						
12285282	Bracket, alternator	1790 Eng	2/5, 3 P (V, T)	3/12, 3 P (V, T)						
12286282	Disk assembly, compressor rotor	M60	3/11, 3 P (V, T)							
12287034	Pin	M60	1/28, 3 P (V, T)	1/29, 3 P (V, T)	1/30, 3 P (V, T)	2/5, 3 P (V, T)	2/27, 3 P (V, T)			

(continued)

TABLE 3. (continued)

Part No. (if available)	Part description (if available)	Vehicle or engine where part is used	1st Test	2nd Test	3rd Test	4th Test	5th Test	6th Test	7th Test	Comments
12287035	Pin, hinge	M60	1/30, 3 P (V, T)	2/27, 3 P (V, T)	3/13, 2 P (V, T)					
12288274A			3/11, 3 P (V, T)	3/12, 3 P (V, T)						
12288274C			3/11, 3 P (V, T)	3/12, 3 P (V, T)						
12288275			3/11, 3 P (V, T)	3/12, 3 P (V, T)						
12288300			3/11, 3 P (V, T)	3/12, 3 P (V, T)						
12304635	Helical spring	M60	1/23, 3 P (V, T)							
12311033			3/12, 3 P (V, T)							
12324433			3/12, 3 P (V, T)							
	Door knob, threaded		1/29, 3 P (V, T)							
	Fuel cell cover	M60	1/30, 3 P (V, T)	2/27, 3 P (V, T cc)	3/13, 2 P (V, T)					
	Fuel tank screw cap		2/27, 3 P (V, T)							
	Heater part	M60	2/28, 3 P (V, T)							
	Latch for telescope	M551	2/28, 3 P (V, T)							
	Plunger on escape hatch	M551	2/27, 3 P (V, T, cc)							

(continued)

TABLE 3. (continued)

Part No. (if available)	Part description (if available)	Vehicle or engine where part is used	1st Test	2nd Test	3rd Test	4th Test	5th Test	6th Test	7th Test	Comments
	Solenoid plate	M60	2/27, 3 P (V, T, cc)							
	Spring, 2" long		2/19, 3 P (V, T)	3/11, 3 P (V, T)						
	Spring, 7" long		2/19, 3 P (V, T)	2/27, 3 P (V, T)						
	Thin cylinder, 3- 3/4" diameter		2/27, 3 P (V, T, cc)	2/28, 3 P (V, T)	3/13, 2 P (V, T)					3/13 Thin on interior of cylinder
	Tube, hollow, 12" long, 3/4" diameter		2/19, 3 P (V, T, cc)	3/15, 2 P (V, T)						
	Tube, hollow, 9" long, 3/4" diameter		2/19, 3 P (V, T, cc)							

I. RUN SUMMARY

[illegible]

Figure 4. Completed Ivadizer Run Data Sheet.

Figure 4. (continued).

II. PARTS RUN

Part No.	Part description (shape and function)	Quantity of parts	Are any two part dimen- sions greater than five inches?	Are there any holes, cavities, or unusual configurations? If so, describe.
8761080	Eye, engine lifting M60	1	No	No
8761088	Curved pipes, drain pipe M60	1	No	No
10527981	Threaded ring for telescope mast	3	No	No
10865283	Flange, intercyliner camshaft sleeve	1	No	No
10882773		1	No	No
11684019	Plate, mounting, fuel with supporter	1	No	No
11682768	Bracket, cooling for support	1	No	No
12275712	Bracket, solenoid	6	No	No
11684160	Support, fuel injection	1	No	No
10873682		1	No	No
11684156	Plate, fuel injection tube clamp	1	No	No
12254297	Spacer	1	No	No
12288300		2	No	No
12283742	Lever	2	No	No
11684234	Brackets, cooling fan shroud	1	No	No
12286282	Disc assembly, compressor rotor	2	No	No
12288275		1	No	No
8761088	Curved steel pipe, drain pipe	2	No	No
12288724A			No	No
12288274C	2" springs	3	No	No
10955921	Lever, door, cupola	3	No	No

Figure 4. (continued).

III. IMMEDIATE POST RUN EVALUATIONS

Part No.	Any apparent deficiencies, obvious thin areas, voids, non-adhering; if so, describe with locations on part
	The curved steel pipe had a black discoloration. Peening removed it.

Figure 4. (continued)

IV. POST RUN TESTING

Part No.	Thickness, mils (range)	Locations of thin areas (less than specification)	Salt spray Hour of testing, P/F	Chromate conversion or other post-treatment (P/F); if fail, describe failure and possible reasons
8761080	0.37 to 0.9			
8761088		Black, disappeared after peening		
10527981	0.5 to 0.8			
10865283	0.5 to 0.8			
10882773	0.5 to 0.8			
11684019	0.6 to 0.8			
11682768	0.6 to 0.9			
12275712	0.4 to 0.6			
11684160	0.3 to 0.8			
10873682	0.5 to 1.0			
11684156	0.7 to 1.0			
12254297	0.6 to 0.9			
12288300	0.5 to 0.9			
12283742	0.6 to 0.8			
11684234	0.3 to 0.4			
12286282	0.4 to 0.6			
12288275	0.5 to 1.0			
8761088	0.5 to 1.0			
12282274A	0.8 to 1.0			
12288274C	0.7 to 0.9			
2" springs	Ok vinyl			
10955921	0.5 to 1.0			

DISCUSS DEFICIENCIES AND FAILURES ON REVERSE SIDE, GIVING AS A MINIMUM, PART NUMBER AND DESCRIPTION, NUMBER OF PARTS AFFECTED, LOCATION ON PART, HOW SUSPENDED FROM THE PLATING RACK, CLEANING TECHNOLOGIES, ETC., AND POSSIBLE REASONS FOR THE DEFICIENCIES AND FAILURES.

The second sheet (II. Parts Run) lists the parts that were processed in the run identified by quantity, part number, part description, functional description (two inch spring, for example), or by shape (curved steel pipe, drain-pipe). Also recorded were whether the part had any two dimensions greater than five inches (requires processing in two steps), and whether there were any holes, cavities, or unusual configurations that would require special processing.

The third sheet (III. Immediate Post Run Evaluations) provides an opportunity to list any apparent deficiencies or problems. On this run, the curved steel pipe (Part Number 8761088) had a dark black surface color. This color was removed by peening with glass beads, and the pipe had a satisfactory, shiny, metallic appearance.

The fourth sheet (IV. Post Run Testing) describes tests run on the parts after coating. In this run, the coating thickness was measured on the parts and was expressed as a range from thinnest to thickest. At least three thickness measurements were made on each part. (The two inch spring was an exception. The magnagauge probe could not make adequate contact with the thin metal coil.) All areas on all parts had at least the minimum thickness for a Class 3 coating, 0.3 mils.

The fourth sheet also provided space for listing other tests, such as applying chromate conversion coatings and adhesion. Aluminum coatings were always acceptable with respect to accepting chromate conversion and the coating sticking to the metal. Figure 4 presents a completed Ivadizer run data sheet.

ECONOMIC ANALYSIS

The economic analysis of the Ivadizer is discussed in five parts: hazardous waste disposal and wastewater treatment costs, employee protection costs, capital costs, and annual cost.

A. Hazardous Waste Disposal and Wastewater Treatment Costs--

The cadmium plating facility at Anniston Army Depot provided the

basis for estimating quantities of hazardous waste generated by cadmium electroplating, capital costs, and annual costs. Estimates for other Army facilities could be made by comparing the facility with Anniston.

ANAD has two cadmium plating lines; an automatic line and a manual line. The automatic line is more economic and more efficient and is used whenever possible. The automatic line contains 1,100 gallons of plating solution. The manual line has two 1,800 gallon tanks and three 480 gallon tanks for a total of 6,140 gallons of plating solution. Representative concentrations are four ounces of cadmium and 20 ounces of cyanide per gallon.

ANAD purchased 2,500 pounds of cadmium and 1,600 pounds of sodium cyanide during 1990. Cadmium was consumed as electroplated coatings or lost to wastewater and electroplating hazardous waste. Cyanide was lost to wastewater, electroplating hazardous waste, and air emissions since cyanides are hydrolyzed to volatile hydrogen cyanide ($\text{CN}^- + \text{H}_2\text{O} \rightarrow \text{HCN} + \text{OH}^-$) during the plating process.

It was assumed that of the 1,600 pounds of cyanide, 100 pounds were lost as air emissions and 1,500 pounds reported to hazardous waste and wastewater. For 1990, ANAD plated an estimated 40 baskets of parts per day and operated 238 days. Assuming each basket of parts had eight square feet of surface and the average coating thickness was 0.0005 inches or 0.5 mils, about 1,700 pounds of cadmium left the Depot as electroplated coatings and 800 pounds reported to hazardous waste and wastewater (see Figure 5).

The ANAD cadmium electroplating facility generated 14,677 pounds of hazardous waste and 250,000 gallons of wastewater during 1990, disposed of at a cost of \$98,590 (see Figure 5). ANAD's cadmium electroplating waste disposal costs reflect treatment requirements necessary to meet Federal and Alabama standards. In other states and municipalities, these costs could be different since each state and sometimes each municipality has the option of imposing more stringent regulations which could in

**ESTIMATED QUANTITIES OF CADMIUM AND CYANIDE REPORTING
TO HAZARDOUS WASTES AND WASTEWATER AT
ANNISTON ARMY DEPOT DURING 1990**

(a) Cadmium in product

Pounds of cadmium in product = $8 \frac{\text{sq. ft.}}{\text{basket}} \times 40 \frac{\text{baskets}}{\text{day}} \times \frac{238 \text{ days}}{\text{year}}$
 $\times \frac{1 \text{ foot}}{12 \text{ inches}} \times 0.0005 \text{ inches} \times \frac{62.4 \text{ pounds}}{\text{cubic foot}}$ of water $\times 8.642 \text{ dens-}$
 ity of cadmium = $1,711 \frac{\text{pounds}}{\text{year}}$ -- say, 1,700 pounds

(b) Cadmium in hazardous waste

Cadmium to hazardous waste and wastewater = $2,500 - 1,700$
 = $800 \frac{\text{pounds}}{\text{year}}$

(c) Cyanide

Cyanide purchases = $1,600 \frac{\text{pounds}}{\text{year}} - 100 \frac{\text{pounds}}{\text{year}}$ as air emissions
 = $1,500 \frac{\text{pounds}}{\text{year}}$ to hazardous waste and wastewater.

(d) Cadmium electroplating waste disposal cost

14,677 pounds of hazardous waste at \$0.50 per pound	\$ 7,340
250,000 gallons of wastewater at \$0.365 per gallon	<u>91,250</u>
TOTAL	\$98,590

(e) Employee protection costs

Quarterly monitoring of area and employees	\$ 6,400
Semiannual blood tests (30 employees)	3,000
Upgraded annual medical exam (30 employees)	<u>6,000</u>
TOTAL	<u>\$15,400</u>

Figure 5.

crease these disposal costs.

B. Employee Protection Costs--

OSHA requirements for employees exposed to cadmium are expected to become more stringent. This is also a cost factor. By analogy for existing regulations for lead exposure, employee medical and exposure monitoring cost could be \$15,400 annually (see Figure 5). Proposed cadmium exposure limits are more stringent than those now existing for lead and employee protection costs could be significantly higher.

C. Capital Costs--

Table 4 compares capital costs for an Ivadizer system and a cadmium electroplating facility. Estimated capital costs are \$1,025,000 for the Ivadizer system and \$600,000 for the cadmium electroplating facility. The capital cost estimates do not include degreasing, cleaning, stripping, and rinsing facilities that are common to both the Ivadizer and cadmium electroplating. The Ivadizer capital cost estimate is based upon actual costs incurred while installing an Ivadizer system at ANAD in August and September 1990. The cadmium electroplating facility cost estimate was based upon vendors' estimates for a facility similar to the current ANAD electroplating facility.

The cadmium electroplating facility cost is estimated based upon the present EPA regulations for cadmium and OSHA regulations for lead. More stringent regulatory requirements would, at best, significantly increase capital costs and, at worst, render cadmium plating infeasible.

Retrofitting a cadmium plating facility to achieve zero wastewater discharge standards would be expensive. Scientific Control of Chicago, Illinois,⁽²⁾ provided an estimate of \$300,000 to \$400,000 for a facility the size of ANAD. The cost would be very situation-specific. Designing and engineering the system would be a significant effort and expense. A new cadmium plating

**TABLE 4. CAPITAL COST COMPARISONS BETWEEN
ALUMINUM COATING AND CADMIUM ELECTROPLATING**

		Source
A. Aluminum Coating		
Ivadizer Model HR72X144	\$ 437,500	Actual Sales Price (ASP)
Two additional parts coating racks	57,600	ASP
Barrel coating parts rack	28,500	ASP
Two grit blasting cabinets	77,000	ASP
Cryogenic cooling system	35,000	ASP
Two glass bead peening cabinets	77,000	ASP
Recommended spare parts	40,900	ASP
Manufacturer's installation and training	92,200	ASP
Customer supplied facility modification and freight	<u>179,300</u>	IT and ANAD estimate
TOTAL CAPITAL COST	\$1,025,000	
B. Cadmium Electroplating		
1100 gal. automatic cadmium electroplating system	\$ 310,000	Vendor's quote
Two 1800 gal. cadmium plating lines	100,000	Vendor's estimate
Three 480 gal. cadmium plating lines	60,000	Vendor's estimate
Customer supplied facility modifications and freight	<u>130,000</u>	IT estimate
TOTAL CAPITAL COST	\$ 600,000	

facility that had to conform with zero discharge standards would cost about as much as an Ivadizer.

However, the choice facing most Army installation is whether to replace an existing cadmium plating facility with an Ivadizer. For that case, a reasonable assumption would be that the cadmium plating facility can be converted to another use at its present depreciated value.

D. Annual Costs--

Table 5 compares annual costs of an Ivadizer system and a cadmium electroplating facility. Annual costs per square foot plated are \$6.77 for aluminum and \$4.55 for cadmium. These costs do not include degreasing, cleaning, stripping, and rinsing facilities that are common to both the Ivadizer and cadmium plating. The Ivadizer costs are based upon operating experience at Titanium Finishing, Inc.⁽³⁾ Cadmium plating costs are based upon operating experience at ANAD and medical and monitoring test expenses equivalent to those incurred for employee lead exposures. The capital recovery is based on interest paid on U.S. Treasury securities; a higher interest rate would probably be appropriate for a private sector facility.

ANAD's cadmium plating facility has the advantage that the wastewater can be treated in the Depot wastewater treatment plant and meet EPA standards. A plating facility that had to have a separate wastewater treatment facility or a zero discharge facility to satisfy more stringent wastewater discharge standards would have a much higher per gallon of wastewater treatment cost.

Table 5 shows that about one-third of the annual costs for cadmium plating are attributable to hazardous waste treatment and disposal and employee protection. These costs will be higher whenever local environmental and health regulatory agencies impose more stringent standards or if future federal requirements become more stringent.

**TABLE 5. ANNUAL COST COMPARISONS BETWEEN
ALUMINUM COATING AND CADMIUM ELECTROPLATING**

Annual Costs of the Ivadizer	
Day shift labor, 3 people, \$20/hr, 2080 hr/year	124,800
Night shift labor, 3 people, \$22/hr, 2080 hr/year	137,280
Maintenance, 2% of capital cost	20,500
Insurance, 1% of capital cost	10,250
Utilities, \$10/hr, 3800 hr/year	38,000
Wire, \$6.50/hr, 3800 hr/year	24,700
Boats, \$9/hr, 3800 hr/year	34,200
Capital recovery, 9%, 15 years	<u>125,850</u>
Total Annual Cost	515,580
Annual Costs of Cadmium Plating	
Day shift labor, 3 people, \$20/hr, 2080 hr/year	124,800
Maintenance, 2% of capital cost	12,000
Insurance, 2% of capital cost	6,000
Utilities, \$1/hr, 1900 hr/year	1,900
Cadmium metal, \$5.015/lb, 2500 lb/year	12,540
Sodium cyanide, \$1.15/lb, 1600 lb/year	1,840
Capital recovery, 9%, 15 years	73,670
Hazardous waste disposal, 14,700 lb at \$0.50/lb	7,350
Wastewater treatment, 250,000 gal/year at \$0.365/gal	91,250
Employee cadmium exposure monitoring	6,400
Blood tests for cadmium	3,000
Increment annual physical exam costs	<u>6,000</u>
Total Annual Costs	346,750
$\text{Square feet plated} = 40 \frac{\text{loads}}{\text{day}} \times 8 \frac{\text{sq. ft.}}{\text{load}} \times 238 \frac{\text{days}}{\text{year}} = 76,160 \frac{\text{sq. ft.}}{\text{year}}$	
Cost per sq. ft. plated - Aluminum	$\frac{515,580}{76,160} = 6.77$
Cadmium	$\frac{346,750}{76,160} = 4.55$

CONCLUSIONS

Aluminum coatings could replace most cadmium electroplates using existing procedures and specifications. Procedures and specifications for threaded fasteners could be modified so that aluminum could replace cadmium. Aluminum coatings will provide better corrosion protection than cadmium.

Aluminum coatings are now more expensive than cadmium electroplates. However, anticipated regulations will increase the cost of hazardous waste treating and health regulations for cadmium electroplating facilities. Additionally, as more Ivadizers are installed and the technicalities of using them become refined, the Ivadizer per part cost is expected to be reduced. Thus, the forecast is that Ivadizer coatings will become more cost competitive with cadmium electroplating.

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EVALUATION OF A FLUIDIZED BED
PAINT STRIPPING AND DEGREASING SYSTEM AT
RED RIVER ARMY DEPOT

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for the United States Army Toxics and Hazardous Materials Agency*

WHAT IS A FLUIDIZED BED PAINT STRIPPER?

A fluidized bed paint stripper (FBPS) uses heat to remove paint, grease, and oil. Heating to between 600 and 800°F converts paint to a char which is easily removed by abrasive blasting and other techniques (low to medium pressure water wash, steam cleaning, detergent wash, low energy abrasive blasting, brushing, etc.). Grease and oil are pyrolyzed (burned) and appear as the products of combustion (carbon dioxide, water vapor, SO₂, particulate, etc., depending on the composition of the grease and oil). The process does not require the use of chlorinated solvents either for degreasing or paint stripping. Consequently the FBPS eliminates air emissions and hazardous wastes caused by the use of chemical solvents.

The Red River Army Depot's (RRAD) fluidized bed uses aluminum oxide particles that have the size and consistency of sand. The particles are suspended in a stream of compressed air that



moves upward just fast enough to keep the particles suspended without blowing them out of the bed. Due to the fluid-like nature of the bed, the heat transfer media is able to provide a high heat transfer rate (approximately that of a liquid). Consequently, painted parts can be heated to operational temperatures faster than can be accomplished with an atmospheric oven.

Figure 1 is a schematic representation of the FBPS at RRAD. The fluidized aluminum oxide is heated by external electric heaters. The electric heaters provide better temperature control than would be provided by a combustion process. Temperature control is vital to controlling the fluidizing air density and velocity and maintaining the bed in a fluidized state. Figure 2 is a photograph of a fluidized bed.

The air velocity through a fluidized bed is low -- of the order of 1 to 10 feet per second. This can be compared with a 100 to 500 feet per second particle velocities for abrasive cleaning. Additionally, the volume of air used to fluidize the bed is small (approximately 30 scfm). This means that (1) in a fluidized bed, there is little, if any, abrasive action on the parts being cleaned and (2) there is insufficient air to burn the organic matter in the paint, oil, and grease. Therefore, an after burner is used to provide the high temperature necessary to insure complete combustion of the pyrolyzed organic material from the processed parts.

After immersion of the part in the hot fluidized bed and complete pyrolysis of the organics, the part is moved from the hot to the cold bed (Figure 3). In the RRAD system, the parts are cooled in a water jacketed fluidized bed which can cool parts from 800°F to ambient temperature in 30 minutes.

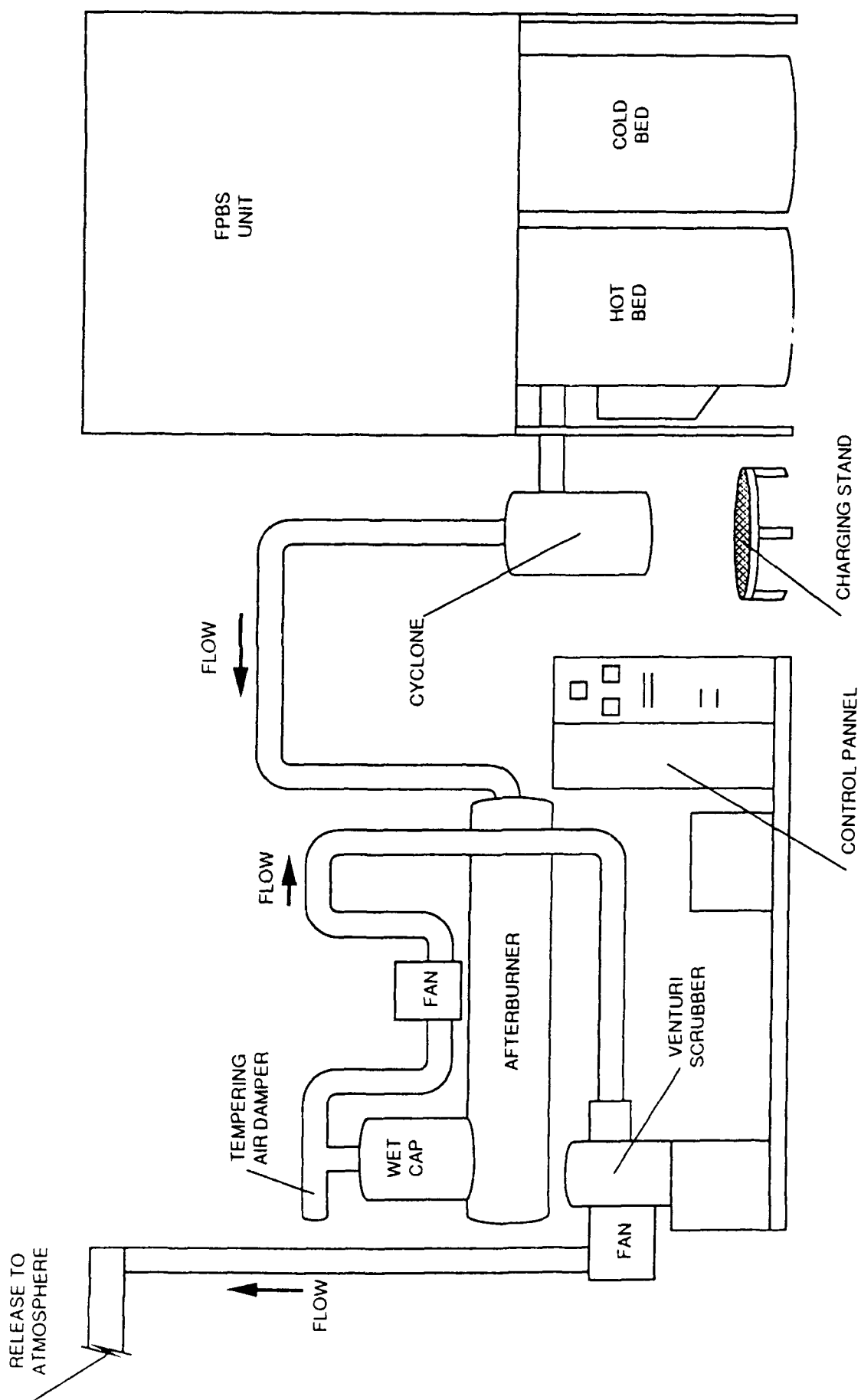


Figure 1. Schematic representation of the RRAD FPBS unit.

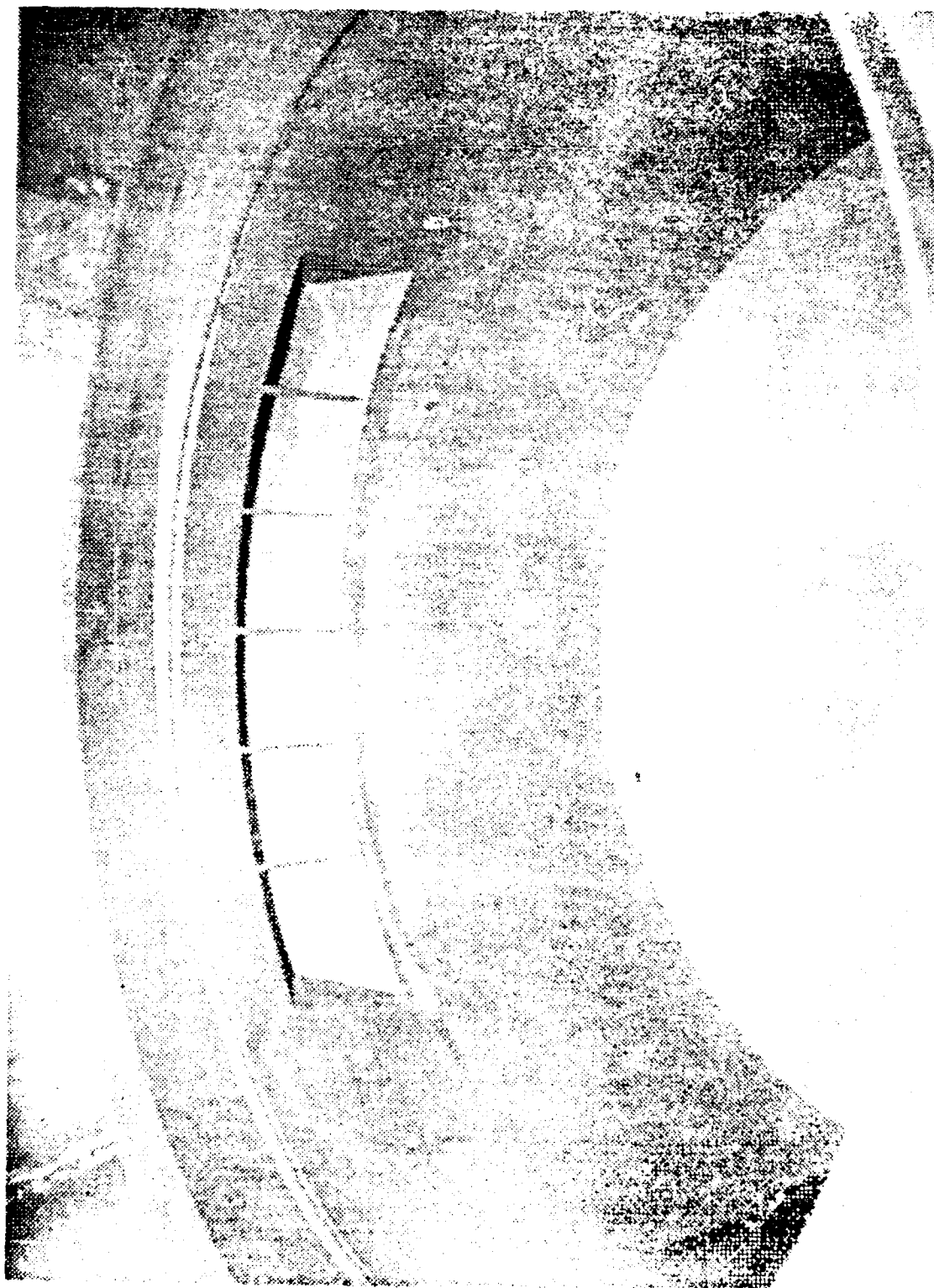


FIGURE 1. Photograph of Flutitized Bed showing the almost fluid-like surface of the sand, the large air "bubbles" breaking the surface and the "ripples" where a "bubbled" broke.

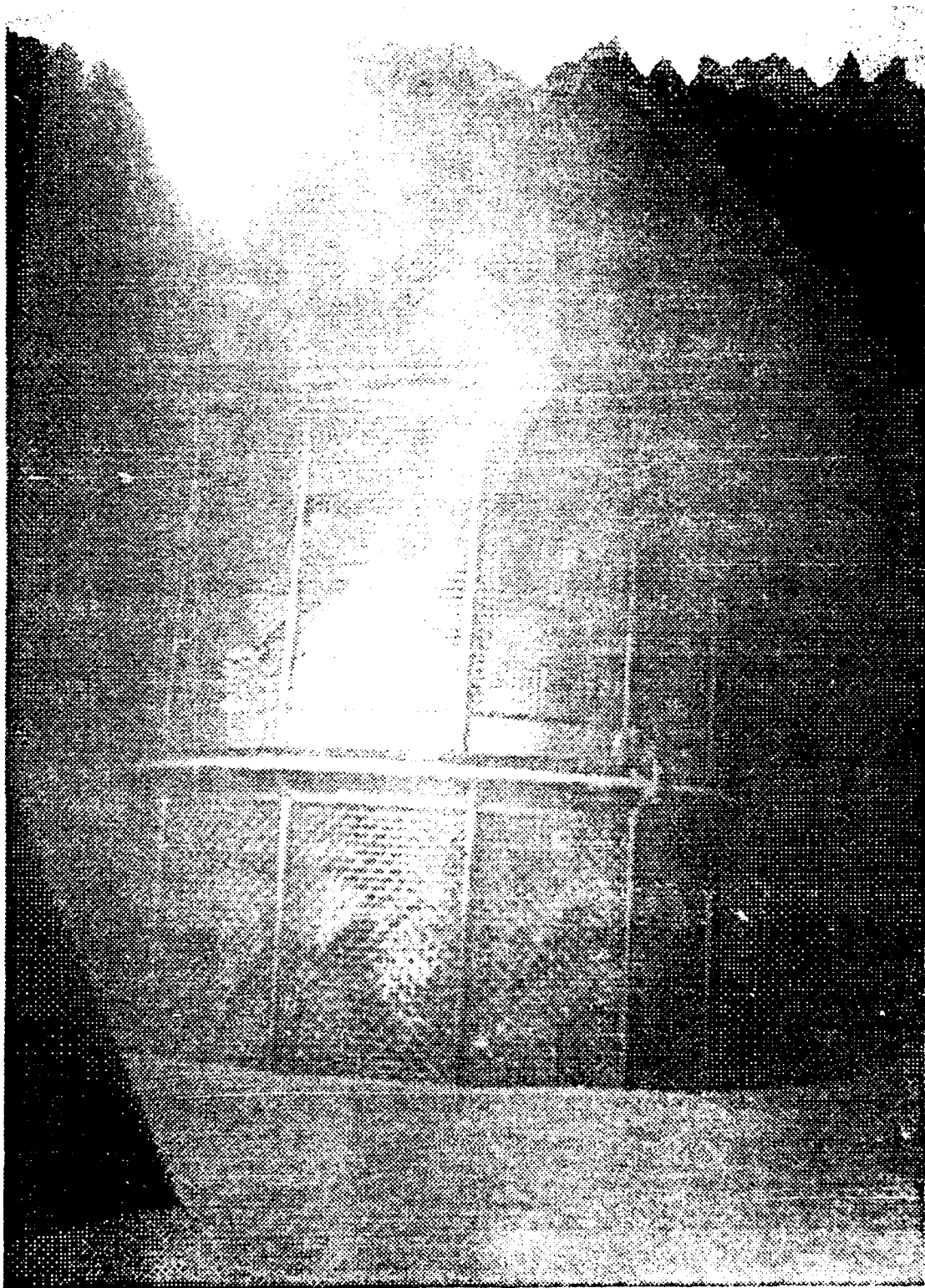


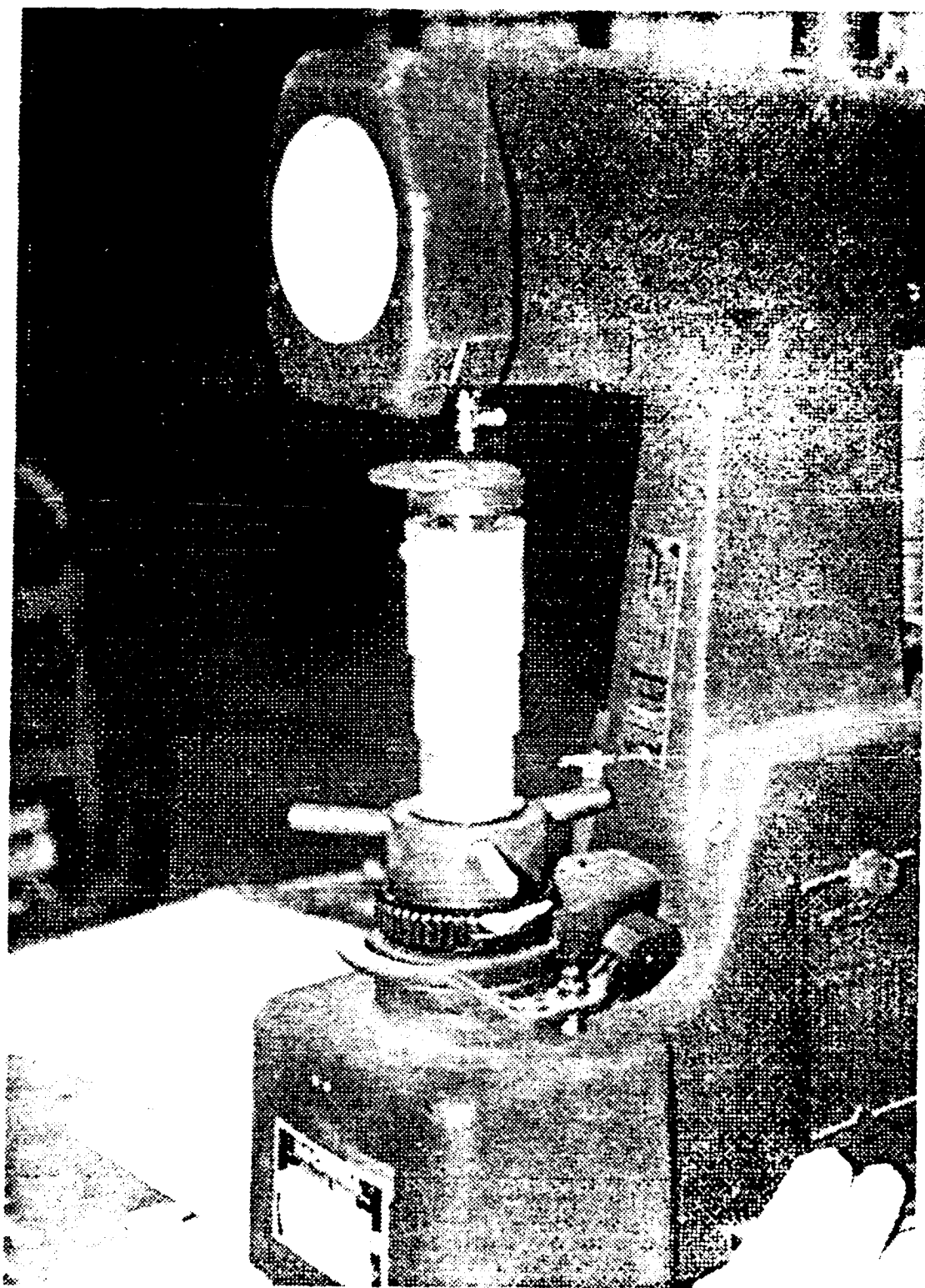
Figure 1. Photograph of parts being tested in the test facility.

TEST PROCEDURES

Virtually any part unaffected by the operating temperatures of the fluidized bed (600 to 800°F range) and contamination by the aluminum oxide in the fluidized bed can be processed. At the normal FBPS operation temperature of 600 to 800°F potential problems are dimensional changes (warping, stretching, distortion, etc.) in parts, and changes in the parts mechanical properties (heat treatment). Also requiring evaluation is retention of aluminum oxide on the parts or in recesses or curvatures.

Parts at RRAD were evaluated using two methods: a material sciences/engineering design analysis, or an experimental/physical examination. Where there was sufficient information on the metallurgy and configuration, the decision to process the part could be made from that data. Where insufficient data was available, an experimental approach was used to determine if the part could be processed in the FBPS. For these undefined parts material hardness and part dimensions were used as indicators of FBPS effect.

For the initial screening, part hardness was measured with minimal preparation. This provided a method of detecting gross changes in part hardness without having to prepare sectioned metallurgical samples. Figure 4 is a photograph of a hardness test on a part. After processing in the FBPS, another hardness measurement was made and part dimensions were compared to a control part. This allowed detecting gross changes in the overall dimensions or hardness of the part. Parts with significant changes in hardness or dimensions were categorized as not suitable for FBPS processing. Parts with a 10 percent or less change in hardness were tested further. Further testing required sectioning the part so that a true measure of the part hardness before and after processing in the FBPS could be made. If no changes in hardness occurred on sectioned part samples, then the part was considered suitable for processing in the fluidized bed. From the experiments, a body of test data on various metals was assembled. From that data, extrapolation to other parts was done



using the material science/engineering and design analysis method.

The work at RRAD revealed that all the aluminum parts processed at the Red River Army Depot are in some way either work hardened or heat treated. The testing on the FBPS showed that the heat treatment or work hardening in the aluminum parts is lost at the fluidized bed paint stripper operating temperatures. Therefore, all the aluminum parts investigated at RRAD are not FBPS candidates without some downstream processing to restore heat treatment. Additionally, parts that contain low melting metals (less than 600°F), are not suitable for processing in the FBPS these parts are damaged by processing in the FBPS and could possibly damage the FBPS.

Analysis of the aluminum oxide after six months of operation shows that some heavy metals are present (Table 3). Analysis of virgin aluminum oxide established that the aluminum oxide was initially free of the heavy metals.

Cadmium and zinc are commonly used as corrosion protection coatings on steel parts. Most of the protective coatings encountered at RRAD were electroplated cadmium and zinc. Cadmium and zinc melt at temperatures lower than the operating temperature of the FBPS. As liquids, they could drip off the parts and fall into the bottom of the fluidized bed, coating the fluidizing plate at the bottom of the bed and affecting the flow of fluidizing air. Additionally, some of the metal will volatilize at the FBPS operating temperatures and leave the bed in the air stream as atmospheric emissions. Since airborne cadmium and zinc represent significant health hazards, specific efforts were made to determine the fate of these metals in the FBPS process. The tests conducted demonstrated that; 1) less than 1% of the cadmium and zinc processed are being removed in the FBPS from the parts processed, 2) that the fluidized bed (aluminum oxide) has become contaminated with both metals, 3) the cadmium and zinc are being released as atmospheric emissions and in the scrubber water, and 4) metals buildup in the aluminum oxide fluidized bed will make

the bed media a hazardous waste.

ATMOSPHERIC EMISSIONS TESTING

There is a low pressure drop venturi scrubber on the discharge of the fluidizing bed exhaust. Atmospheric emissions tests detected small amounts of heavy metals in this exhaust (Table 1). Likewise, some heavy metals were detected in the scrubber water discharge (Table 2).

During test 2 there were approximately 2 lb of cadmium and 4.8 lb of zinc on the parts processed in the FBPS. Emissions test 2 revealed: air emissions of 3.7×10^{-5} lb of cadmium and 1.9×10^{-5} lb of zinc, and water emissions of 3.2×10^{-5} lb of cadmium and 6.6×10^{-4} lbs of zinc. Additionally, approximately 2.4×10^{-5} lb of cadmium and 9.7×10^{-5} lb of zinc were deposited in the cyclone dust and 0.084 lb of cadmium and 0.04 lb of zinc were added to the fluidized beds. The air and water emissions represent only .003% of the charged cadmium and .014% of the charged zinc. The vast majority (99%) of the cadmium and zinc charged into the FBPS remain on the parts.

Stripping and cleaning remove cadmium and zinc coatings in down stream processing, typically with abrasive blasting and/or acid cleaning. Therefore, the FBPS has minimal effect on the hazardous waste generation from down stream processing. However, it produces some new cadmium and zinc emissions streams (the stack gases, cyclone dust, waste fluidized bed material, and scrubber water).

The atmospheric release of cadmium and zinc does not occur simultaneously with the processing of the cadmium and zinc in the FBPS. During test 2 when nearly 7 pounds cadmium and zinc were processed and emissions of cadmium and zinc were only marginally more (2.2×10^{-5}) than during test 3, when no cadmium and zinc were processed. This implies that the cadmium and zinc are removed from the parts during processing, retained in the fluidized bed, and gradually released.



TABLE 1. ATMOSPHERIC EMISSIONS OF PARTICULATE AND METALS

Test No.	Date (1991)	Particulate emissions			Metals emissions							
		Concentration		Mass emission rate, lb/h	Concentration, $\mu\text{g}/\text{m}^3$				Mass emission rate, lb/h			
		gr/dscf	mg/m^3		Cd	Cr	Pb	Zn	Cd	Cr	Pb	Zn
1 ^a	2/26	0.13	297.5	0.80	30	373	574	861	7.9E ⁻⁵	9.7E ⁻⁴	1.5E ⁻³	2.2E ⁻³
2	2/26	0.007	15.8	0.047	12.4	<4 ^b	17.6	<7	3.7E ⁻⁵	<1.1E ⁻⁵	5.2E ⁻⁵	<1.9E ⁻⁵
3	2/27	0.004	8.2	0.024	6	<2.8	4.9	<4.7	1.8E ⁻⁵	<8.4E ⁻⁶	1.4E ⁻⁵	<1.4E ⁻⁵
4	2/27	0.0037	8.4	0.023	<2.1	<3.2	3.7	<5.3	<5.9E ⁻⁶	<8.8E ⁻⁶	1.0E ⁻⁵	<1.5E ⁻⁵
5	2/27	0.013	28.8	0.083	2.2	<2.9	10.1	34.5	6.3E ⁻⁶	<8.2E ⁻⁵	2.9E ⁻⁶	9.9E ⁻⁵
6	2/28	0.0037	8.4	0.024	9.3	<2.9	16.1	4.8	2.6E ⁻⁵	8.2E ⁻⁶	4.5E ⁻⁵	1.4E ⁻⁵
7	2/28	0.0028	6.4	0.019	<1.9	10	18.8	14.4	5.5E ⁻⁶	2.9E ⁻⁵	5.4E ⁻⁵	4.2E ⁻⁵
8	2/28	0.0040	9.1	0.026	12.4	<3	9.5	13.8	3.5E ⁻⁵	<8.4E ⁻⁶	2.7E ⁻⁵	3.9E ⁻⁵

^aTest 1 is considered nonrepresentative because of a scrubber upset. It does provide an indication of potential uncontrolled emissions.

^b"Less than" denotes below method detection limit (MDL).

TABLE 2. WATER SAMPLE ANALYSES RESULT

Test No.	Parts Charged	Metals Concentration, $\mu\text{g/l}$			
		Cadmium	Chromium	Lead	Zinc
2	956 lbs of cadmium and zinc plated steel parts and scrap aluminum	0.004	0.083	ND	0.082
3	None	0.002	0.030	0.0041	0.031
4	Scrap aluminum	ND	0.007	0.0007	0.021
6	964 lbs of cadmium and zinc plated parts and scrap aluminum	0.007	0.064	ND	0.20

ND - None Detected

HAZARDOUS WASTE MINIMIZATION POTENTIAL

The objective was to assess the fluidized bed process as an alternate to chemical paint stripping and chlorinated solvent degreasing. Chemical paint stripping and degreasing operations use toxic agents and generate hazardous waste sludges and other toxic environmental emissions. The sludges from chemical-cleaning and paint stripping also may contain heavy metals from the paints removed and from the cadmium and zinc and/or lead leached from the part during the cleaning process.

To evaluate the hazardous waste generation potential of the FBPS, it was necessary to identify the chemical stripping and cleaning processes affected by the FBPS. The cleaning shop, after degreasing, segregates parts into ferrous and non-ferrous for paint stripping. The ferrous parts are stripped in a caustic paint stripper and the non-ferrous parts in a methylene chloride paint stripper. These two paint stripping processes generate significantly different wastes because of the different stripping agents. The caustic stripper can be neutralized with acids and thus made less hazardous. The methylene chloride contamination is more toxic and presents more difficult handling and disposal problems.

The FBPS evaluation program eliminated aluminum parts as candidates for the FBPS. The aluminum parts are processed in the methylene chloride stripper. That process stream still exists and is unaffected by the FBPS operation.

As previously discussed, the FBPS will not totally replace the degreaser or caustic stripper, but its use will reduce the quantity of waste generated from these operations. The current estimate is that the FBPS will be capable of processing 20 to 40 percent of the ferrous parts processed in the degreaser and caustic paint strippers. Therefore, the FBPS will proportionally reduce the quantity of hazardous waste generated from those chemical cleaning processes.



TABLE 3. SAND SAMPLE ANALYSES RESULTS

Sample description	Concentration, µg/g							
	Cadmium		Chromium		Lead		Zinc	
	Before	After	Before	After	Before	After	Before	After
Virgin sand drum #16864	ND	NA	9.8	NA	0.7	NA	2.9	NA
Cold fluidized bed sand	1.7	2.8	13	15	18	23	16	22
Hot fluidized bed sand	5.5	26.7	24	14.3	23	25.9	34	38.4
Cyclone dust	NA	40.4	NA	35.1	NA	77.5	NA	161

ND - Nondetectable

NA - Not applicable

In exchange for this 20 to 40 percent reduction, a fluidized bed system (two beds of the current size) with the capacity to process these parts would annually generate 8,000 pounds of aluminum oxide waste. The FBPS will also have some air emissions of heavy metals and a wastewater stream with a heavy metal contamination. The aluminum oxide waste from the fluidized bed is probably a hazardous waste because of the heavy metals contamination. Most of the inorganic paint residue remains on the part after the FBPS processing and is removed in downstream processing similar to the existing processing.

Red River Army Depot records show that in 1990, 210,493 pounds of sludges and wastes were generated from those two operations (caustic paint stripping and degreasing). Therefore, the reduction potential is approximately 65,000 pounds per year of sludges based on a 30 percent reduction in parts processed through those operations.

Those sludges are typically disposed of at a cost of \$0.66 per pound for stripper sludges (Waste Inventory Item No. 3,310) and \$1.15 per pound for degreaser sludge (Waste Inventory Item No. 4,593). Therefore, the FBPS has the potential for a savings of \$51,900 in hazardous waste generation, in terms of sludge disposal cost.

The FBPS generates waste aluminum oxide (fluidizing bed media) that cost an estimated \$2,000 annually for disposal based on the fluidizing media lasting a minimum of two years. Additionally, the fluidizing bed media breaks down due to sand components rubbing against each other. There is an estimated 150 pounds or 1 ft³ of dust generation per month. The analysis of the dust indicates there is heavy metal contamination and it is probably a hazardous waste. It is a relatively small quantity and could easily be mixed in with sludges from the chemical cleaning operations and disposed of as hazardous waste or accumulated and disposed of when the bed is replaced. The quantities of hazardous materials associated with down stream refinishing procedures for parts processed in the FBPS are nearly identical to chemical str-

ipping operations.

WATER USAGE FOR THE SYSTEM

The system as designed and installed at Red River Army Depot is not optimized to minimize water usage. Water usage could be reduced by using the cooling water from the cooling bed as the scrubber and quench water supply. The reduction would be significant. For the current system, water usage is approximately 20 gpm (approximately 16 gpm to waste water and 4 gpm evaporated). If the cooling bed water stream were in series with the quench and scrubber water flow rather than in parallel, water usage would be cut to approximately 10 gpm and the wastewater flow would be approximately 6 gpm. At 6 gpm, the annual disposal cost of the wastewater through the chemical treatment plant at RRAD is \$15,500 based on a treatment cost of \$0.03 per gallon, six hours operation per day, five days per week, and 48 weeks per year.

COMPARISON WITH OTHER THERMAL PAINT REMOVAL METHODS

There are three thermal paint removal systems currently available: fluidized bed, atmospheric ovens, and molten salt baths. All three of these use heat and a controlled (oxygen deficient) oxidizing environment to pyrolyze and oxidize the organic contaminations on metal parts. All operate at similar temperatures (600 - 800°F) and operating times range from 30 minutes to 6 hours. The parts produced by all three require down stream processing before refinishing. Atmospheric, water, and solid waste emissions are significantly different as are operating problems (except that all require handling hot parts).

The atmospheric furnace has the advantage of not contaminating the parts with aluminum oxide which can be trapped in cavities and recesses. Its main disadvantage is poorer heat transfer. Consequently, the atmospheric furnace is slower than an FBPS with cycle times of six hours per batch versus the fluidized bed cycle time of two hours, including cool-down time.

The problems associated with the effect on metallurgy are similar to the FBPS except that with the atmospheric furnace it is more difficult to control and maintain an oxygen-deficient combustion environment and pyrolysis conversion of the organic materials. As a consequence, the organics may burn, creating hot spots that could possibly damage the metal parts because of the excessive temperatures. However, the atmospheric furnace does not contaminate parts with the fluidizing bed medium (the aluminum oxide). Therefore, processed parts are a little easier to handle downstream from the cleaning operation.

Atmospheric emissions are about the same from both furnaces and the downstream emissions control system requirements are the same. Typically, atmospheric furnaces exhaust at high temperatures (no water quench following the after burner) than the FBPS. The requirement for a pollution control device on the exhaust to remove material carried out of the system is dependent on local environmental regulations. However, there is slightly more particulate generation in the fluidized bed because of the breakdown of the fluidizing media.

In molten salt baths, various types of molten salt mixtures can be used for the removal of specific organic coatings. For example, RRAD uses this process for removal of rubber from tactical equipment parts. The temperatures of operation of a molten salt bath cause many of the same problems with metallurgy as the FBPS. The molten salt bath does not have the aluminum oxide contamination problem like the FBPS. It does require a rinsing operation which creates an additional wastewater stream. Atmospheric emissions from the molten salt bath would be similar to the FBPS. However, there are fewer products of combustion since some oxidation takes place chemically in the salt bath with little or no atmospheric emissions. However, the chemical oxidation generates a sludge in the salt bath that requires continuous removal.

Fluidized beds have been used extensively for cleaning plastic injection dies and miscellaneous automotive parts. The atmospheric furnace and molten salt baths are used extensively by en-

gine rebuilders. The atmospheric furnace is the cheapest to purchase and easiest to operate of the three types of thermal furnaces. However, the molten salt bath produces the best cleaning with the simplest down stream processing of the three. The fluidized bed is the least likely to cause chemical damage to parts.

Each cleaning system has a unique set of benefits and liabilities. None of them are a universal replacement for chemical degreasing and/or paint removal. All three systems have capital costs greater than an equivalent capacity chemical cleaning system. Because of their high temperature (600°F plus) operation, all the processes will potentially damage some parts currently processed in the chemical cleaning systems at RRAD.

CONCLUSIONS

The fluidized bed rapidly heats and cools part and while controlling the atmosphere around the parts thus preventing ignition and temperature excursions on the part's surfaces. Rapidly bringing parts to the bed operating temperature results in a short pyrolysis cycle and pyrolyze the organics on the surface of the parts makes them easier to prepare for repainting.

The FBPS is an alternative to some chemical degreasing, cleaning and paint removal operations. However, it can only be used for specific parts. The FBPS is one of three commonly used thermal processes (molten salt bath, atmospheric furnaces, and fluidized bed pyrolysis) used as a replacement for chemical paint stripping and degreasing.

The FBPS provides for an approximately 30 percent reduction in the weight of hazardous waste generation from the chemical cleaning and paint stripping operations. The reduction would provide a net savings of approximately \$35,000 annually in the cost of hazardous waste disposal. The estimated cost of one additional fluidized bed to meet the required capacity needs at RRAD is approximately \$600,000 (including semi-automatic handling equipment). Operating cost for labor and utilities for two oper-

ating units of the size installed at RRAD would be approximately \$60,000 annually. Assuming a capital recovery factor of .124 (15 years @ 9 percent) the capital recovery of the additional unit is approximately \$75,000 for a net increased annual cost of \$100,000 to process approximately 30 percent of the parts processed at RRAD.

DISCLAIMER

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Treatment of Contaminated Soil in
Two-Stage Incinerator

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ABSTRACT

The two-stage incinerator permits one-step treatment of soils contaminated with both organic as well as inorganic contaminants. The two-stage incinerator combines advances in fluidized-bed incinerator technology with those of cyclonic incinerator technology. This advanced incinerator, while efficiently destroying organic contaminants, encapsulates inorganic contaminants within benign, glassy agglomerates suitable for disposal in an ordinary landfill.

Agglomerates have been produced in a bench-scale unit (BSU) at several different operating conditions with samples of both "clean" and spiked soil. The agglomerates are firmly consolidated and have a dark brown to black, glassy appearance. Tests to determine the leaching characteristics (TCLP) of the agglomerates have also been performed. Initial tests indicated that the inorganic contaminants are found to be concentrated primarily in the fine particulate elutriating from the fluidized bed and collected in the cyclone. Future tests will emphasize returning these fines into the fluidized bed for assimilation with the agglomerates.

Introduction

A single-step treatment for soils contaminated with both organic as well as inorganic contaminants is being developed at the Institute of Gas Technology (IGT) under the co-sponsorship of the U.S. Environmental Protection Agency (EPA), the Gas Research Institute (GRI), and IGT's Sustaining Membership Program. The new technology has promise of surpassing the economic as well as efficiency benefits of many competing technologies.



The Two-Stage Incinerator

The two-stage fluidized-bed/cyclonic agglomerating incinerator (TSI), shown schematically in Figure 1, is based on combining fluidized-bed agglomeration and cyclonic combustion technologies. This two-stage combination results in an extremely flexible incinerator for the treatment of contaminated soils. The system can operate over a wide range of conditions. In the system, the organics contained in the soils are efficiently destroyed ($>99.99\%$ Destruction and Removal Efficiency (DRE)), while residual solid inorganic contaminants are agglomerated within a glassy matrix, being rendered benign and suitable for disposal in ordinary landfills.

The first stage of the incinerator is a sloping-grid, agglomerating fluidized-bed reactor that can operate under either substoichiometric or excess air conditions. In addition to the sloping grid, the first stage incorporates a central jet and a classification section. Fuel gas and air enter the central jet while only air is admitted through the grid and the classifier. The contaminated soil is introduced directly into the fluidized bed. With a unique distribution of fuel and air, the bulk of the fluidized bed is controlled at a temperature of 1500° to 2000°F , while the central spout temperature can be varied from 2000° to 3000°F . The hot zone thus formed is localized and very distinct in terms of temperature and size, and can be altered by changing the gas-flow distribution. This feature is the key to its ability to produce benign agglomerates and to control the rate of discharge from the fluidized bed.

Upon the introduction of contaminated soil into the fluidized bed, the organic fraction is immediately volatilized and partially combusted. The inorganic contaminants, depending upon particle size and volatility will either be retained in the fluidized bed or get carried over with gas. The fraction of these contaminants that remain behind are subjected to the "hot zone" treatment where they undergo melting and subsequent agglomeration along with the soil in which they are present and are entrapped in the very soil matrix. Once the particles leave the hot zone and transit through the bulk of the bed, they resolidify. The process of melting, agglomeration, entrapment, and resolidification continues in the fluidized bed until the agglomerates grow large enough and dense enough to find their way down the classification zone. Generally, the agglomerates grow to a maximum size of about 1/2 inch.

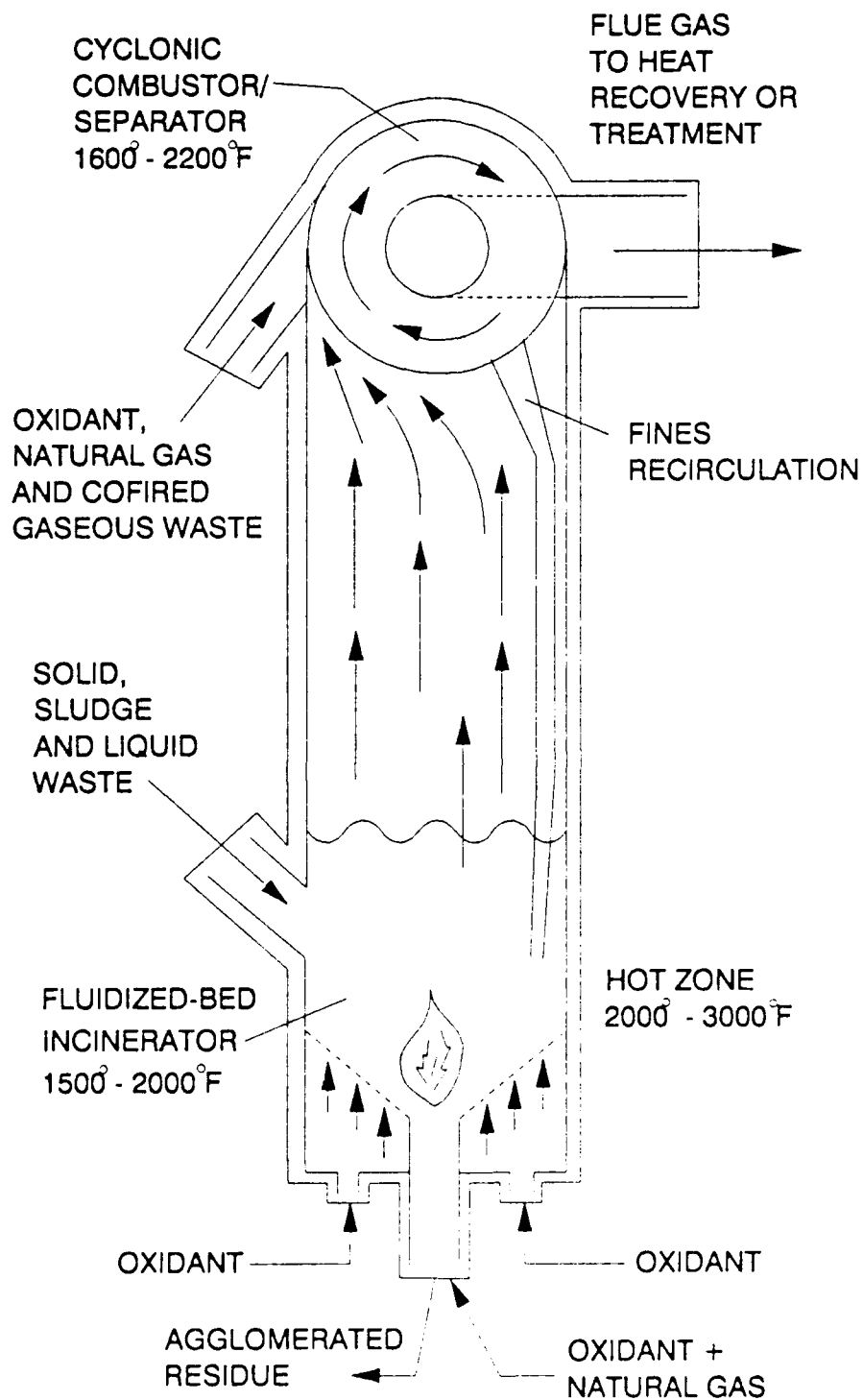


Figure 1. IGT's TWO-STAGE FLUIDIZED-BED CYCLONIC AGGLOMERATING INCINERATOR



These agglomerates are essentially nonleachable and, therefore, can be safely disposed of in ordinary landfills.

The fine particulates elutriated from the fluidized bed are generally rich in inorganic contaminants. They can be collected in the cyclone and separately treated for contaminants, or returned to the fluidized bed for ultimate assimilation with the agglomerates.

The volatile organic compounds are incinerated in the second stage of the two-stage incinerator. This second stage is a cyclonic incinerator, which provides intense combustion of these organic compounds. Either secondary air or a mixture of natural gas and air is fed to the cyclonic incinerator to maintain a temperature in the range of 1600° to 2400°F. The cyclonic combustor provides sufficient residence time at these operating conditions to combust all the organic compounds and carbon monoxide to carbon dioxide and water, yielding a DRE in excess of 99.99%.

The resultant gaseous effluent from the cyclonic incinerator is cleaned by utilizing available technologies such as scrubbers, filters, etc.

The application of a two-stage incinerator developed in this program is primarily targeted for the remediation of contaminated soils at Superfund sites; however, it has a much broader scope. The two-stage incinerator will find numerous beneficial applications in the combustion and treatment of municipal solid wastes, municipal sewage sludge, hospital wastes, pulp and paper mill sludge, rubber tires, nonmetallic automotive scrap, wood by-products, biomass and agriculture wastes, petroleum coke, high sulfur coals, and various hazardous wastes.

The two-stage incinerator is a novel approach to staged incineration/combustion technology (1) with the following unique features:

- No moving parts are needed for agglomerate withdrawal
- It permits utilization of methane injection to minimize gaseous pollutants
- It allows introduction of sorbents and/or additives to enhance capture of inorganics
- Heat input may be easily recovered and utilized
- It can handle solid, sludge, liquid, and gaseous wastes

- It agglomerates and encapsulates inorganic contaminants in the first stage, with final destruction of organic compounds in the second stage
- It insures high DRE despite upsets or spikes in the fluidized bed
- It insures efficient utilization of natural gas.

Background Data

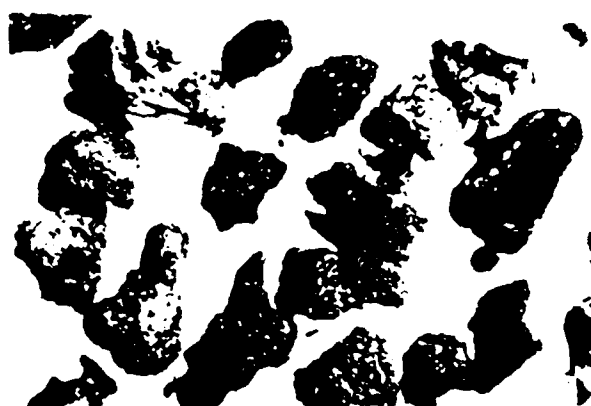
The two-stage incinerator concept is based primarily on combining IGT's fluidized-bed ash agglomeration/gasification technology with the cyclonic combustion technology. Both of these technologies have demonstrated superior performance in the area of waste treatment.

Performance of First Stage Fluidized-Bed Incinerator

The ability of first stage fluidized-bed incinerator technology to produce agglomerated ash from coal has been amply demonstrated during the development of the U-GAS coal gasification process. The U-GAS process incorporates agglomeration as the method of discharging ash from the fluidized bed. The U-GAS process development tests were conducted in a 3-foot diameter reactor equipped with a sloping grid, a jet for creating a hot zone within the fluidized bed, and an ash discharge nozzle similar to the one proposed here. Fluidization was maintained by steam or mixtures of steam, oxygen, and air. The hot zone was established by introducing streams of air or steam enriched with oxygen into the central jet. The localized zone of relatively high temperature resulted from the reaction of oxygen with carbon and hydrogen present in the coal. In tests with coal, the addition of supplemental fuel was not necessary.

As particles of ash within the hot zone were heated to temperatures above their softening points, their surfaces become sticky. Collisions with other particles resulted in particle growth through accretion. As the agglomerates grew in size, the fluidizing gases could no longer support them in the bed. Thus, agglomerates were removed from the bed via a terminal-velocity mechanism. During the development of the U-GAS process, many types of coals (2,3) were tested in the 3-foot diameter unit to determine the effects of different ash properties (composition and softening temperature) on agglomeration characteristics. Agglomerates produced from the ash of different feedstocks are shown in Figure 2. When subjected to the EP Toxicity Test (EPA 1310), these agglomerates were found to be in compliance with the

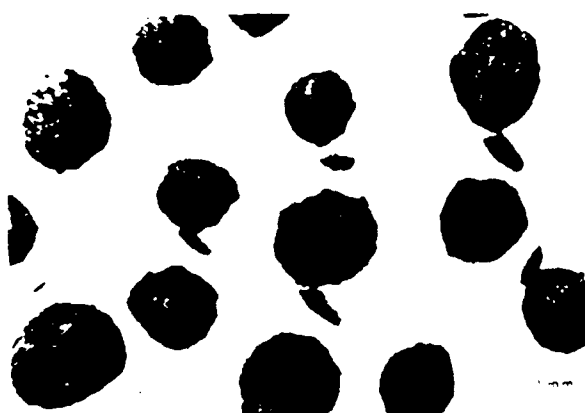




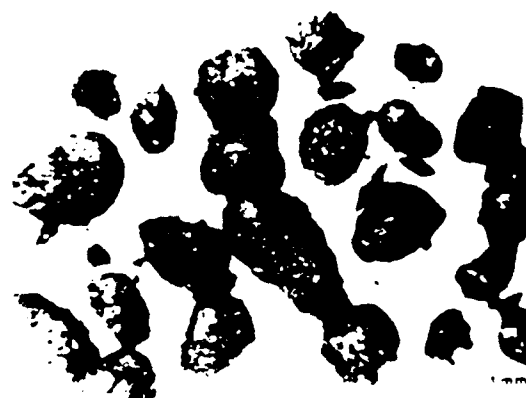
(a) Illinois No. 6



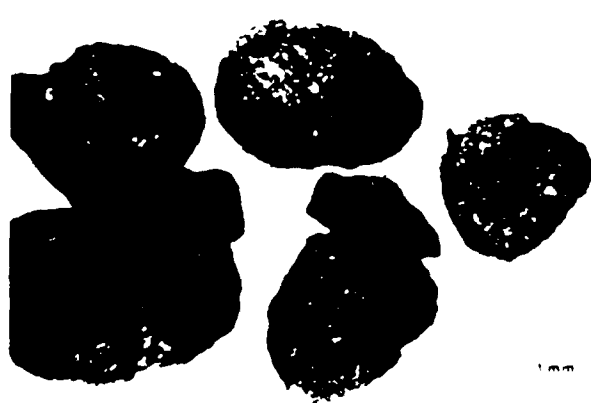
(b) Kentucky No. 9 coal



(c) Metallurgical coke - 1800 F



(d) Kentucky No. 9 coal - 1800 F



(e) Metallurgical coke - 1800 F



(f) Kentucky No. 9 coal - 1820 F

Figure 2. TYPICAL ASH AGGLOMERATES FROM DIFFERENT COAL FEEDSTOCKS

regulations. The encapsulation of trace inorganic metals from coal in glassy, essentially nonleachable ash agglomerates can be readily extended to the treatment and incineration of other wastes. Another important aspect was that despite the presence of abundant organic material in coals, the agglomerates were completely devoid of any organic compounds -- indicating that the fluidized bed, while producing agglomerates, is capable of stripping off organics from the waste. These organics are partially combusted in the fluidized-bed stage; the balance in the cyclonic stage.

In another application, IGT is developing a thermal process for reclamation of spent blasting abrasives from U.S. Naval shipyards (4). Each year, the eight U.S. Naval shipyards produce about 100,000 tons of spent blasting abrasive during repainting operations, which must be reclaimed or otherwise disposed of. This is one of the major hazardous waste streams generated at Naval shipyards. Paint and rust removed from the surface of the ship during blast cleaning, as well as marine biota (crustaceans, seaweed, etc.), accumulate in the spent blast abrasive. Occasionally, material from other vessel servicing operations accumulates as tramp with the spent blast abrasive. Because of this contamination and the generation of fines during blasting, the spent blast abrasive is not reusable. The used blast abrasive is either stockpiled onsite, or, in some states, is landfilled at special hazardous waste sites.

IGT conducted bench-scale and pilot plant-scale fluidized-bed tests with samples of spent blasting abrasive (provided by the U.S. Navy) contaminated with copper-based or tributyl tin (TBT)-based paints. The tests were conducted at bulk-bed temperatures of 1470° to 1500°F with five different samples of spent abrasives (either coal ash slag or copper smelter slag-based abrasive). Complete analyses for organics, total and soluble metals, major oxides, and size distribution for the feed and output streams from the calciner tests were performed. Analyses for organics, organotin, total tin, and size distribution were also conducted for the coal/TBT test. The results of these analyses indicated that the reclaimed materials were suitable for reuse in blasting operations. Further, Modified Method 5 sampling of the stack gas during the coal/TBT test confirmed that the calciner destroyed TBT to greater than 99.99%.



Reclaimed abrasive was returned to the U.S. Navy in bulk for performance evaluation. The performance of the reclaimed abrasive was comparable to that of fresh abrasive. The results demonstrated that the sloping-grid fluidized-bed (SGFB) calciner produced reclaimed abrasives conforming to the requirements of MIL-A-22262A for fresh blasting abrasives.

Because the preliminary economic evaluation for spent blasting abrasive reclamation using the SGFB calciner was very favorable, the U.S. Navy has decided to proceed with the design, construction, and operation of a 3-ton/hour prototype calciner at a Navy shipyard.

In a similar project, IGT employed the SGFB calciner to reclaim used foundry sand for an automobile manufacturer. Tests with the reclaimed foundry sand demonstrated comparable performance to that of new foundry sand (5).

Development of the Cyclonic Combustor Second Stage

The cyclonic combustor which constitutes the second stage of the two-stage incinerator has been extensively tested at IGT. Tests have been conducted with CCl_4 -- a PCB (polychlorinated biphenyl) surrogate -- as well as liquid wastes and a low-Btu gas. The cyclonic combustor readily destroys organic compounds with high DRE and also minimizes emissions of carbon monoxide and hydrocarbons.

CCl_4 was selected the surrogate material for testing PCB incineration capability in the cyclonic combustor, because it is generally believed to be more stable than PCB's, has a lower relative toxicity, and will not result in products of incomplete combustion that are highly toxic.

To determine the DRE of CCl_4 , high-temperature gas samples were drawn from the combustion system through a Modified Method 5 analytical train, and the residual CCl_4 was trapped in double Tenax beds in series.

In most of the tests, the unit was operated with combustion air preheated to 800°F and a gas firing rate of about 0.8 million Btu/h. The gas sampling probe was located immediately beneath the cyclonic section of the combustor, with a hot-gas residence time of about 0.25 seconds. Temperatures were taken by a suction pyrometer near the exhaust of the combustor base, after a gas residence time of about 0.75 seconds.

The cyclonic combustor tests demonstrated that CCl_4 could be destroyed to greater than six-9's DRE by incineration with methane and preheated air at a residence time of 0.25 seconds. Under these conditions, the emissions of nitrogen oxides (NO_x) were relatively high at 130 to 330 ppm. By reducing the air preheat from 800° to 450°F, NO_x emissions dropped to 60 ppm, but CCl_4 DRE was slightly reduced. Abbasi *et al.* (6) and Crimmins *et al.* (7) provide other test results.

A summary of the contaminants and concentrations subjected to testing in the two separate stages of the TSI are presented in Table 1.

Table 1. SUMMARY OF INDIVIDUAL TESTS CONDUCTED IN THE FLUIDIZED-BED INCINERATOR AND CYCLONIC INCINERATOR

Stage	Feed Material	Contaminant	Supplemental Fuel	DRE, %
Fluidized Bed	Spent Foundry Sand	1-2% organic resins & binders	Natural gas	Up to 98
	Spent Blast Abrasive	1-2% organics, 100 ppm TBT	Natural gas	>99.99
	Coal	Coal, ash, S, organics, metals	None	
Cyclonic	CCl_4	100% pure	Natural gas	>99.9999
	CCl_4	0.5% in Hexane	None	>99.999
	CCl_4	1.0% in Hexane	None	>99.999
	Industrial Wastewater	15-50% dissolved solids, 3270 Btu/lb (HHV)	Natural gas	N/A
	Low-Btu Gas (67 Btu SCF)	9.2% H_2 , 61.3% N_2 , 1.7% CO , 3.7% CO_4 , 24.1% CO_2	None	<50 ppm CO <10 ppm CO_x

Program Objectives

A multiyear program has been undertaken to develop a data base for application of the two-stage incineration technology at Superfund sites. The program entails the development of operating conditions in a bench-scale unit (BSU), the design, construction, and operation of a 6-ton/day pilot plant, and the utilization of the pilot plant data to assess the commercial viability of



of the technology. The primary objectives of the program include identification of operating conditions in the fluidized bed that, for a given contaminated soil, will enhance the capture and encapsulation of inorganic contaminants within the glassy matrix, identification of operating conditions in both stages for the destruction of organic contaminants with a DRE exceeding 99.99%, and the minimization of utility requirements through maximum heat recovery.

In the first phase of the program, a BSU was constructed and operated for the establishment of the operating conditions required for soil agglomeration. Simultaneously, a TSI pilot plant was also designed with construction and operation to proceed during the next phase. The tests conducted in the BSU are described in this paper.

Bench-Scale Soil Treatment Tests

The bench-scale tests were conducted in a 6-inch diameter fluidized-bed reactor (Figure 3). The bottom of the reactor was fitted with a sloping grid, gas distributor including venturi discharge and central burner jet for replicating the hot zone cyclones are installed downstream of the BSU to collect fine particles elutriated from the fluidized bed. A product gas scrubber is also used to capture fine particles that may elude the cyclones. The BSU is equipped with external electric heaters for achieving temperatures up to 2000°F as well as means for preheating feed gases.

The flows of air, natural gas, and oxygen to the burner jet can be used to adjust the flame temperature. Soil discharged from the bed is collected in a 6-inch diameter stainless steel vessel. Thermocouples indicate temperatures at different levels in the fluidized bed including the air preheat and material being discharged. Differential pressure taps located in the bed provide an indication of the bed level during the test.

A retractable thermocouple assembly was installed for sensing flame temperatures at the burner jet. Its normal position is inside the burner tubing at the burner tip; however, it can be extended beyond the tip into the fluidized bed a total of 8 inches. Type K thermocouples were used for the tests.



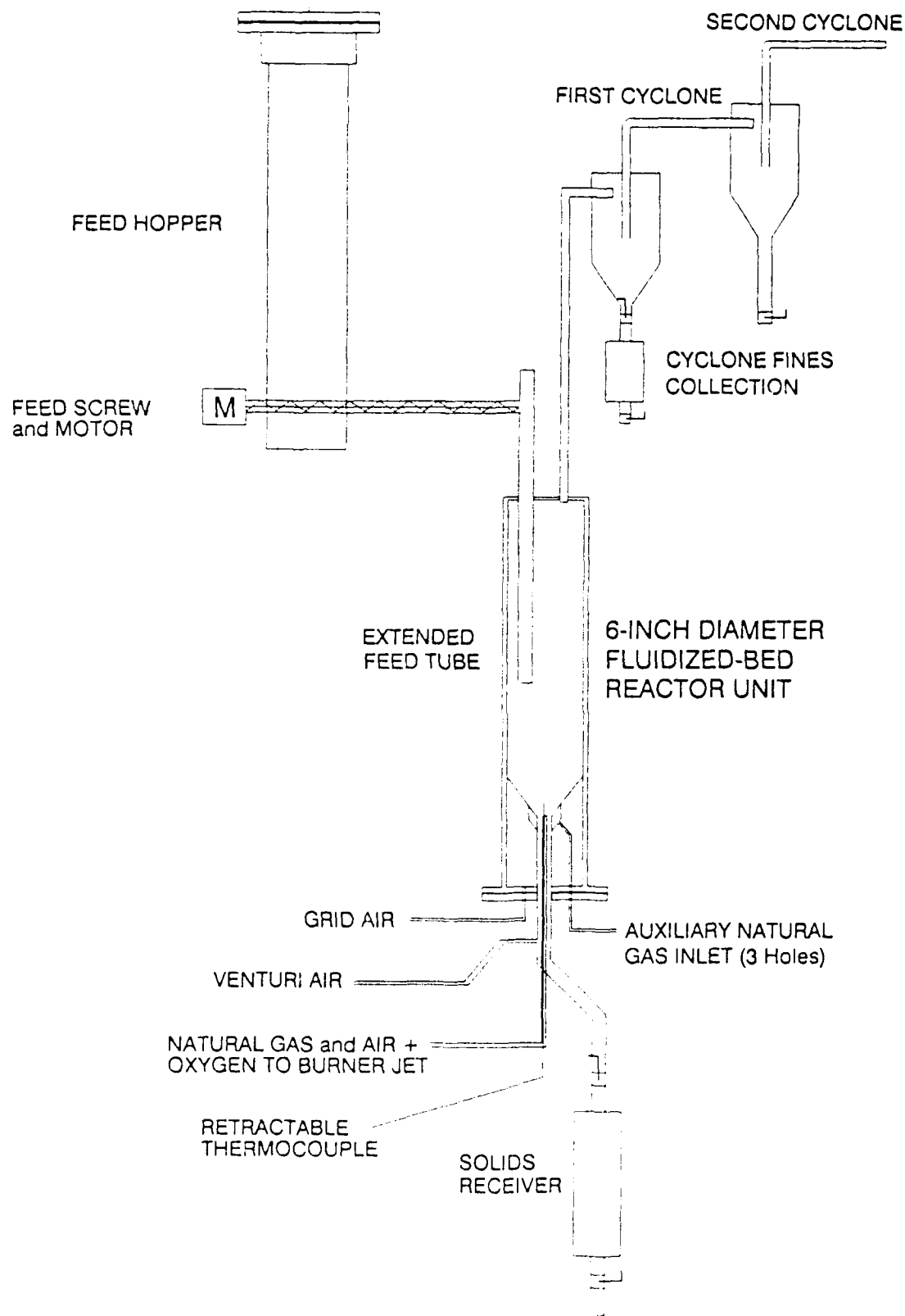


Figure 3. BENCH-SCALE UNIT (BSU)



Preparation of Spiked Soil

The feedstock for the BSU tests was a bulk sample of commercially available "clean" top soil. Grab samples of the soil "as delivered" indicated a moisture content of about 20 weight percent.

About 800 pounds of the soil were dried in a direct-flame rotary dryer. The soil exiting the dryer was in the form of 1/4-inch diameter spheres, which were subsequently crushed and screened to -1/8 inch in a hammer mill.

Grab samples of the dried and crushed soil were taken for proximate and selected elemental analyses. The results of the sample analyses are presented in Table 2. The moisture content of three samples taken after drying averaged 7.9 weight percent (0.25% standard deviation [SD]). The elemental concentrations of arsenic, chromium, and lead averaged 11 (1.7), 32 (2.7), and <10 ppm (0 ppm SD), respectively. These elements were selected based on discussions with the EPA to be the focus of the capture and encapsulation studies. The gross calorific value of the three samples averaged 416 Btu/lb (dry basis) with a SD of 26.5 Btu/lb.

Table 2. CHEMICAL ANALYSES OF DRIED, CRUSHED, AND SCREENED GRAB SAMPLES OF TOP SOIL

Sample No.	<u>1</u>	<u>2</u>	<u>3</u>
Proximate Analysis	-----	wt %	-----
Moisture	7.86	7.65	8.15
Volatile Matter	7.61	7.80	7.81
Fixed Carbon	0.60	0.52	0.48
Ash	<u>83.93</u>	<u>84.03</u>	<u>83.56</u>
Total	100.00	100.00	100.00
Element (dry basis)	-----	µg/g	-----
Arsenic	10	10	13
Chromium	29	34	33
Lead	<10*	<10	<10
Calorific Value	-----	Btu/lb	-----
	390	443	414

* Indicates detection limit of analytical procedure.

The ash fusion temperatures (oxidizing atmosphere) of the three grab samples were also determined and are presented in Table 3. The initial deformation temperature for this sample of top soil is 2400°F; the fluid

Table 3. ASH FUSION TEMPERATURES FOR
BULK TOP SOIL SAMPLE (Oxidizing)

Sample	<u>1</u>	<u>2</u>	<u>3</u>
Ash Fusion Temperature	-----	°F	-----
Initial Deformation	2405	2400	2410
Softening	2515	2502	2510
Semispherical	2620	2600	2620
Fluid	2700+	2700	2700+

temperature is about 2700°F. The initial deformation (softening) temperature provides an indication of the temperatures required for forming agglomerates in the fluidized-bed reactor.

Tests to determine the fluidization characteristics of the soil were conducted in a 6-inch diameter Plexiglas column. The results (Figure 4) showed that the complete fluidization velocity for the -1/8-inch soil sample was 1.25 ft/s.

The initial BSU tests were conducted with the unspiked -1/8-inch soil sample described in Table 2. When soil agglomerates were generated, tests to determine the capture and encapsulation efficiency of the SGFB stage were to be conducted. Because the levels of lead and chromium in the soil were relatively low, the soil was spiked to increase the concentration of these metals to about 90 ppm to facilitate subsequent analyses. The spiking solution contained lead oxide (PbO) and chromium nitrate hydrate [$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] dissolved in nitric acid. The arsenic concentration was about 10 ppm, and no spiking of this carcinogenic material was necessary. A 40 pound batch of soil was carefully weighted into a 30-gallon drum with plastic liner. The drum was placed into a cylinder spinner and rotated at a speed of about 10 rpm and inclined at an angle of about 45°. The spiking solution was slowly sprayed onto the soil sample as it rotated by this procedure. After the solution was applied, three grab samples were taken for chemical analyses to determine the uniformity of the spiking procedures.

The fines fraction (-20 mesh) of the soil was removed by screening prior to spiking. This was done to prevent the spiked soil from being conveyed out of the BSU upon its entry.

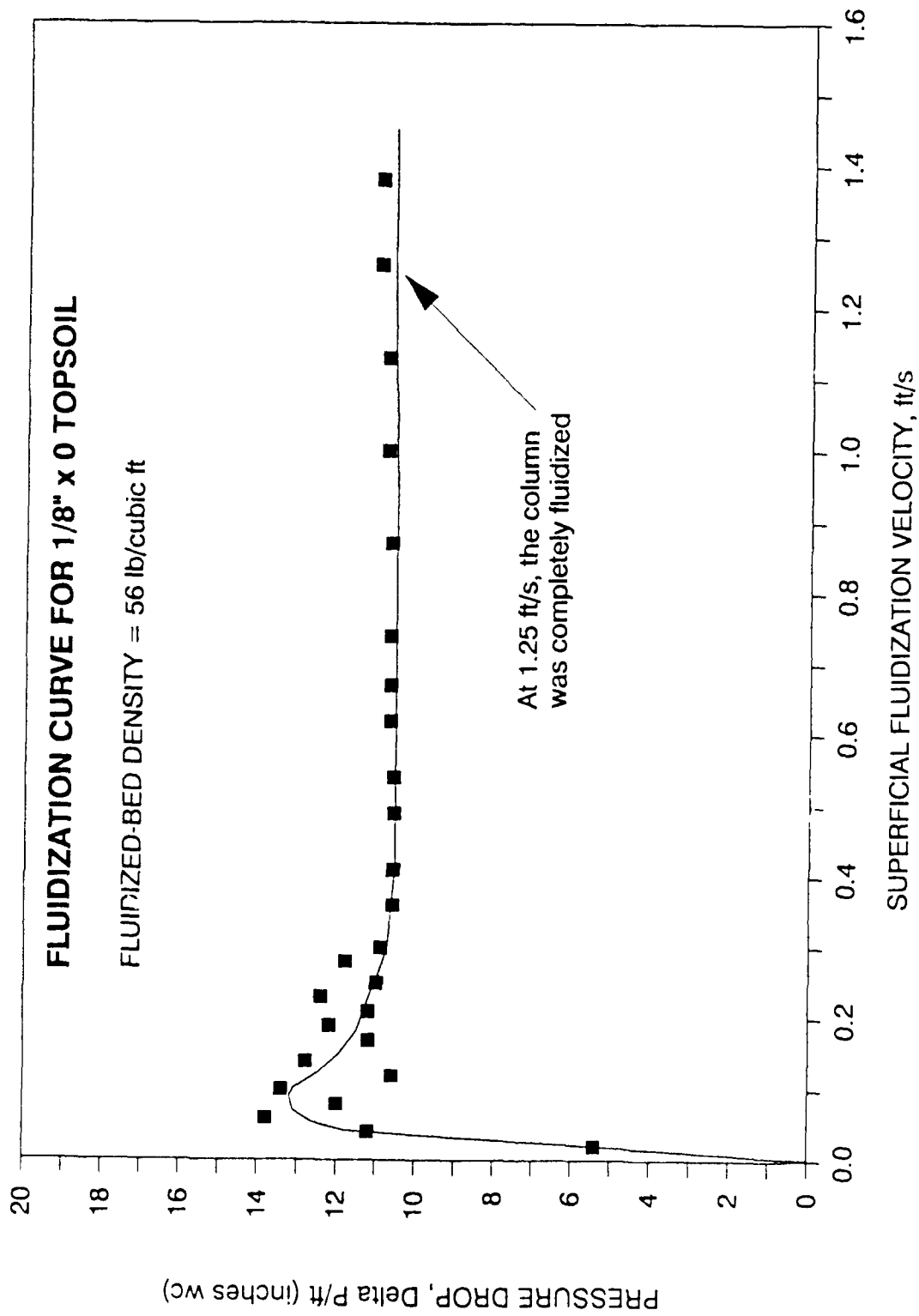


Figure 4. FLUIDIZATION CURVE FOR DRIED AND SCREENED
SOIL SAMPLE (-1/8 INCH)

BSU Tests

A weighed quantity of dried and sized soil was loaded into the feed hopper. Appropriate flows of air were started through the venturi, grid, and burner jet. The BSU temperature was increased to about 1000°F by the electric furnaces. The feed screw was then activated to deliver soil at about 20 lb/h to the BSU. Once the differential pressure taps indicated that a bed had formed, stoichiometric flows of natural gas and air were started to the burner jet. The furnace controllers were then set to the desired temperature for the test. The screw was stopped after about 1 hour of soil feeding. Fifteen pounds of soil yielded a fluidized bed with an aspect ratio (L/D) of about 2, which was suitable for these tests.

Upon achieving the targeted operating conditions, the flow of oxygen to the burner jet was increased incrementally for short periods of time to increase the hot zone temperature. The flow of air was concurrently decreased to maintain stoichiometry. Estimated flame temperatures for natural gas combustion with different enriched oxygen concentrations are presented in Table 4. The flame temperatures exceed the soil fusion temperatures at all oxygen concentrations. However, because of the solids circulation patterns within the fluidized bed, the particles are exposed to the hot zone temperatures for only brief periods. The rate of agglomerate formation and growth must be balanced against the size and temperature of the hot zone.

Table 4. EFFECT OF OXYGEN CONCENTRATION IN AIR ON
THEORETICAL NATURAL GAS FLAME TEMPERATURES*

<u>At Stoichiometric Conditions</u>	
<u>% Oxygen</u>	<u>Temperature, °F</u>
21 (air)	3562
30	4127
40	4520
50	4765
60	4918
65	4976

* Assumes no feed-gas preheat and no
heat loss to surroundings.

The appearance of the material discharged from the venturi provided an indication of the approach to conditions required for soil agglomeration.

Once agglomerates appeared in the discharge, other operating conditions were tested to determine the effects on agglomerate production and quality.

A summary of the operating conditions and qualitative results of the tests conducted in the BSU with "clean" and spiked soil are presented in Table 5. In the first test, operating conditions were established for the fluidized bed to operate between the bubbling and entrained modes. Much of the soil fed to the BSU was entrained into the flue gas. In the second test, the limits of flame temperature were determined with different stoichiometric ratios of natural gas and air entering the jet. However, no apparent hot zone was formed. In Test 3, flame temperatures using oxygen-enriched air were determined. Excessive temperatures generated in the flame damaged the central jet and the retractable thermocouple.

The fourth test was not successful because of a plug in the feed soil dip tube, which caused the feed screw to jam. In the fifth test, a hot zone was formed in the fluidized bed using oxygen-enriched air. The soil was vitrified into a large mass consisting of tiny agglomerates.

Distinct soil agglomerates were first produced in the BSU during Test 6. Figure 5 is a photograph of the agglomerates from this test juxtaposed with a photograph of the feed soil. The agglomerates were of varied shapes and ranged in size from 1/4 to 1 inch. The agglomerates were dark brown to black in color and well consolidated. For comparison, the feed soil was gray and the nonagglomerated material discharged from the BSU was light brown to rusty.

Samples of the raw "clean" soil and agglomerates from this test were analyzed for As and Cr content and subjected to the Toxicity Characteristic Leaching Procedure (TCLP) for As and Cr as well (Pb was below the analytical detection limit as indicated in Table 2). The results in Table 6 show that Cr remained with the soil while As was apparently volatilized. Neither As or Cr was leached into the TCLP extraction media above the detection limit.

In Test 7, a sample of spiked soil was prepared and charged to the feed hopper to test metals capture and encapsulation efficiency. The burner jet was relocated to the side of the venturi to facilitate the removal of agglomerates from the fluidized bed. Many of the same operating conditions from Test 6 were duplicated in this test, however, only a few agglomerates were formed.

Table 5. SUMMARY OF OPERATING CONDITIONS AND RESULTS
OF SOIL AGGLOMERATION TESTS CONDUCTED IN THE BSU

Test No.	2	3	5	6	7*	8*
Bulk Bed Temp, °F	1500	1277	1500	1500	1490	1450
Superficial Fluidization Velocity, ft/s	2.03	1.88	1.96	3.37	3.73	3.36
Burner Jet						
Velocity, ft/s	40	59	132	137	113	99
O ₂ Conc., mol %	21.0	71.6	59.5	47.8	65.7	59.2
Flame Temp (theoretical), °F	3562	5029	4918	4716	4982	4908
Comments	No Aggl.	TC Melt	Vtrfd** Soil	Some Aggl.	Many Aggl.	Good Aggl.
					Few	Good
					Aggl.	Aggl.

* Spiked soil sample.

** Vtrfd. = vitrified.

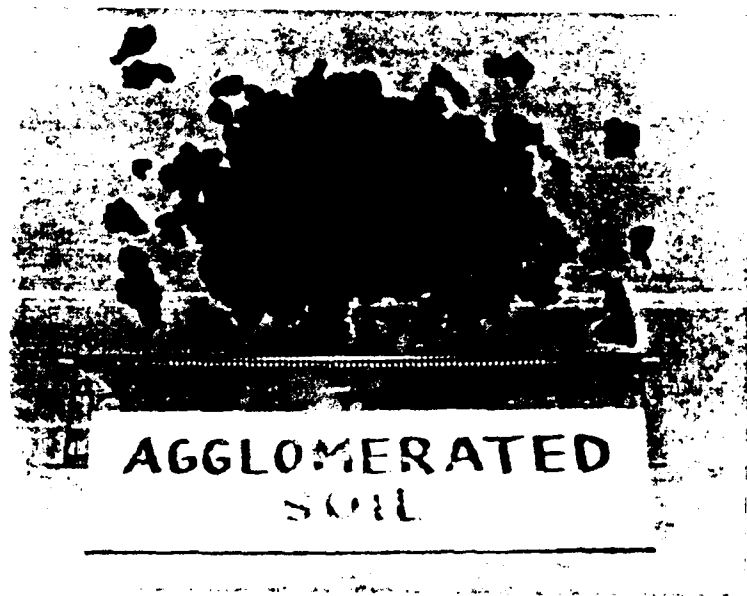


Figure 5. RAW FEED SOIL AND AGGLOMERATED SOIL FROM THE BSI TESTS



Table 6. TCLP RESULTS AND ELEMENTAL ANALYSIS OF
"CLEAN" RAW AND AGGLOMERATED SOIL SAMPLES

Sample	Raw Soil	Agglomerates	TCLP Limit
TCLP Leachate	-----	mg/L -----	
Arsenic	<0.010*	<0.010	5.0
Chromium	<0.050	<0.050	5.0
Element	-----	µg/g -----	
Arsenic	11 (avg.)	<1.0	
Chromium	32 (avg.)	32.9	

* Indicates detection limit of analytical procedure.

In the eighth test, the BSU was returned to the configuration of Test 6. Spiked soil was again prepared and charged to the feed hopper. Agglomerates were again formed from the spiked soil sample in sufficient quantities for detailed analyses. The chemical analyses of the spiked feed soil, agglomerated soil, and cyclone fines from this test are given in Table 7. Samples of the agglomerated soil have been subjected to the TCLP to determine the leachability of As, Cr, and Pb. They were found to be in conformity as shown in Table 8.

Table 7. CONTAMINANT DISTRIBUTION DURING SOIL TREATMENT

Contaminant	Raw Soil	Spiked Soil	Spiked Soil Agglomerates	Fines
	-----	-----	µg/g -----	-----
Arsenic	11	11	<1	8.4
Chromium	32	102	14	266
Lead	<10	95	2	135

Table 8. TCLP TESTS ON SPIKED SOIL AGGLOMERATES

Element	TCLP Leachate	TCLP Limit
	----- mg/L -----	-----
Arsenic	0.001	5.0
Chromium	0.012	5.0
Lead	0.005	5.0

SUMMARY AND CURRENT PROGRAM STATUS

Agglomerates have been produced from a typical sample of soil in a batch BSU that simulates the first stage of IGT's Two-Stage Incinerator. These agglomerates are the first to be formed from soil with the objective of capturing and encapsulating inorganic materials and rendering the contaminated soil essentially nonleachable. The inorganic contaminants tend to concentrate in the fines. These fines can be either treated separately or alternatively returned to the fluidized bed for assimilation with the agglomerates. Some additional work is needed in this area.

The design and specifications for a nominal 6-ton/day two-stage incinerator pilot plant is also complete. The pilot plant design incorporates provisions for feeding natural gas, air, and oxygen to both stages. It will be equipped to test natural gas reburning for emission control. It also has provisions for adequate sampling and on-line analysis. When completed, the TSI pilot plant will be extremely versatile and could be used for testing a variety of soils contaminated with inorganic as well as organic contaminants, and other feedstocks, such as RDF, petroleum coke, and auto fluff.

The two-stage incinerator will be located at IGT's Energy Development Center. The TSI will be installed and connected to existing feeding equipment and downstream product gas cleaning equipment, which include a wet scrubber and bag house.

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DISCLAIMER

Although the research described in this paper has been funded in part by the U.S. EPA, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency and no endorsement should be inferred.

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56WP/soils/RPP



INCINERABILITY RANKING AND SURROGATES FOR
THERMAL DESTRUCTION OF HAZARDOUS WASTE

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ABSTRACT

The U.S. Environmental Protection Agency, Office of Research and Development (EPA/ORD), and the Headquarters Air Force Engineering and Services Center (HQ AFESC) are interested in evaluating the incinerability ranking of principal organic hazardous constituents (POHC's) and surrogate compounds that are used for destruction and removal efficiency (DRE) tests at hazardous waste incinerators. The results of these evaluations will aid development of a more effective and cost-efficient trial burn and performance monitoring process. As a part of the evaluation process, a test was conducted at a full-scale hazardous waste incinerator.

There were two test objectives. The first was to evaluate an incinerability ranking system commonly used by EPA. This system ranks organic compounds based on the gas-phase thermal stability under oxygen-starved conditions and is based on available experimental data. The second objective was to evaluate sulfur hexafluoride (SF_6) as a surrogate for POHC destruction. Sulfur hexafluoride is one of the most stable compounds known with respect to thermal decomposition. Thus, it has been hypothesized that the SF_6 DRE would represent a lower bound to other POHC DRE's in an incinerator. This paper presents the results of the test relative to the two test objectives.

INTRODUCTION

The EPA/ORD and HQ AFESC contracted to Midwest Research Institute (MRI) to evaluate the incinerability ranking of POHC's and surrogate compounds that are used for DRE tests (trial burns) at hazardous waste incinerators. The incinerability ranking evaluated is a thermal stability system developed for EPA by the University of Dayton Research Institute (UDRI). The surrogate compound evaluated is SF_6 . The results of these evaluations should aid development of a more effective and cost-efficient trial burn and performance monitoring process.

Incinerability of POHC's has been measured by a variety of ranking systems, the most common being based on the heat of combustion (Hc) of POHC's, with lower Hc indicating more difficult destruction. The method that has best correlated with field data is the thermal stability ranking system developed by UDRI for EPA. This system ranks POHC's based on their gas-phase thermal stability under oxygen-starved conditions. The ranking is based on a large amount of laboratory-scale experimental data. The experimental data is extrapolated through comparisons of compound structure and properties to obtain a ranking for all POHC's. Evaluation of this ranking system was one objective of this study.

The second objective of this study was to evaluate SF_6 DRE as a conservative indicator for the DRE of POHC's. Since promulgation of the hazardous waste incinerator performance standards in January 1981, there has been a continuing interest in a real-time surrogate compound to measure incinerator compliance with the DRE performance standard. One such possible surrogate is SF_6 . Sulfur hexafluoride is one of the most stable compounds known with respect to thermal decomposition. Thus, it has been hypothesized that the SF_6 DRE would represent a lower bound to other POHC DRE's. Furthermore, SF_6 can be measured at very low concentrations in stack gas on a real-time basis using onsite gas chromatographic techniques. For these reasons, using SF_6 injection with real-time DRE measurement represents a potentially attractive surrogate to determine compliance with DRE performance. Previous field tests conducted to gather data on SF_6 destruction in hazardous waste combustion devices have shown the potential of this compound as a surrogate for POHC destruction, but have not answered all concerns about its use.

The remainder of this paper presents the approach to achieving the experimental objectives, a discussion of the project results, and brief conclusions.

APPROACH

Conducting a full-scale experimental test requires identifying and obtaining permission to test from an operating hazardous waste incinerator. Eastman-Kodak Company's chemical waste incinerator located in Rochester, New York, was identified as a suitable site, and permission was obtained to conduct the test. This incinerator was representative of many currently operating hazardous waste incinerators and was amenable to the variety of

sampling and waste spiking necessary to achieve the project objectives. Kodak personnel provided invaluable flexibility and assistance in operating the incinerator during the test.

The Kodak incineration system treats a variety of combustible liquid and solid wastes generated at the Kodak Park manufacturing site in Rochester. It consists of a rotary kiln, mixing chamber, and secondary combustion chamber, followed by a quench chamber and venturi scrubber. The thermal capacity of the kiln and secondary chamber are a nominal 90 million British thermal units per hour (Btu/h).

An overview of the design of the test matrix conducted at this incinerator is presented in Figure 1. The test was conducted over four days, with the incinerator operating at two different conditions, Condition A and Condition B. Each test condition included 12 sampling periods. Test Condition A entailed operating the incinerator at a high-temperature, low-oxygen condition while firing liquid waste to the kiln. Test Condition B involved operating the incinerator at a low-temperature, high-oxygen condition while firing only liquid and solid wastes to the kiln. The spread in temperature and oxygen concentration between the two conditions was maximized to the extent possible while remaining within acceptable combustion conditions. Temperature was the primary independent variable, while oxygen levels varied as necessary to achieve the desired temperatures.

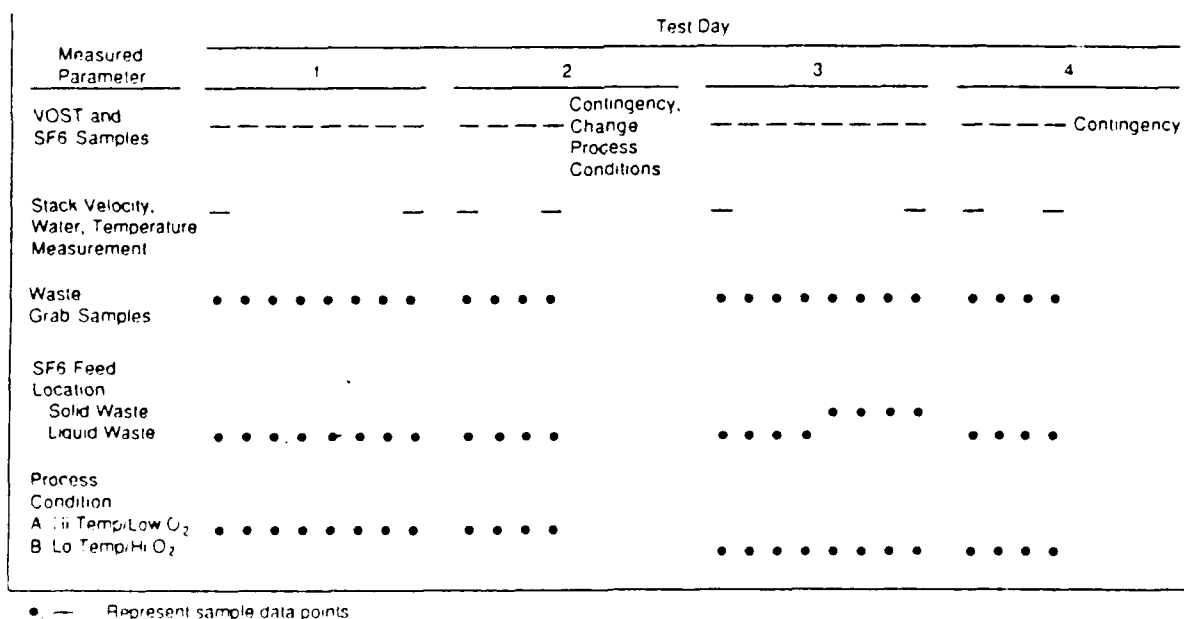


Figure 1. Overview of test matrix.

The wastes used during the test included two liquid organic waste feeds to the kiln and secondary chamber and a surrogate solid waste feed to the kiln. The physical and chemical characteristics of each stream were maintained as consistent as possible throughout the test. Liquid wastes were composed primarily of waste solvent compounds, which were blended to as homogeneous a feed as possible. Solid wastes were bulk sawdust, contained in



35-gallon (gal) fiberpaks. Some auxiliary fuel (No. 2 diesel fuel) was also used during the test.

Six volatile POHC's were spiked to or were native to the liquid waste stream, and one volatile POHC was spiked to some of the solid waste drums. The spiked liquid waste was fed via the kiln liquid waste burner. Table 1 lists the spiking compounds, their thermal stability classification, and the matrix into which they were spiked. These compounds were chosen to represent the five highest of the seven class rankings. Class 1 is the most thermally stable.

TABLE 1. TARGET POHC COMPOUNDS

Compound	UDRI class	Spiking matrix
Monochlorobenzene	1	Liquid waste
Methylene chloride	2	Liquid waste
Tetrachloroethylene	2	Liquid waste
Methyl ethyl ketone	3	Liquid waste
Chloropropene	4	Liquid waste
1,1,1-Trichloroethane	5	Liquid waste
Toluene	2	Solid waste

The SF_6 was spiked into both the liquid and solid wastes during different portions of the test. During days 1, 2, and 4, SF_6 was spiked into the liquid waste fed to the kiln. During day 3, SF_6 was spiked alternately into the solid and liquid waste streams as defined in Figure 1. The SF_6 spiked to the solid waste was microencapsulated, the capsules packaged into 250-milliliter (ml) plastic bottles, and the bottles placed into drums of waste fed to the incinerator. These same drums were the ones spiked with toluene. The SF_6 spiked to the liquid waste was injected as a gas into the liquid waste feed line. The injection point was located upstream of the kiln burner nozzle.

Measurements of the emissions of POHC's and SF_6 were made in a transition duct located between the secondary combustion chamber and the quench. A volatile organic sampling train (VOST), as described in SW-846 Method 0030, was used to collect samples of the POHC's. These samples were analyzed by gas chromatography/mass spectrometry (GC/MS) using selected ion monitoring (SIM). The SIM analysis provided a very low detection limit that allowed quantification of very high DRE's. The SF_6 samples were collected in tedlar bags and analyzed onsite with a gas chromatograph equipped with an electron capture detector. Composite samples of the waste feeds were collected for analysis of POHC's by GC/MS.

RESULTS

This section presents a brief discussion of the process operation followed by the project results. The results are organized by the two project objectives described earlier.

PROCESS OPERATION

Process operation was replicated closely from day to day during the test except for the planned variations in waste feed rates and combustion temperature. Table 2 shows the average values for the key process variables for each of the two test conditions. The waste feed rates were changed to achieve the desired combustion temperature change of about 200°F between test conditions.

TABLE 2. KEY PROCESS OPERATING DATA

Parameter	Units	Condition A	Condition B
Kiln			
Liquid waste feed rate	lb/h	1,760	1,240
Solid waste feed rate	lb/h	0	830
Temperature	°F	1730	1510
Combustion air flow	acfm	7,200	7,220
SCC			
Liquid waste feed rate	lb/h	2,350	2,130
Temperature	°F	1920	1,700
Combustion airflow	acfm	4,330	3,180
SCC exit			
Oxygen	%	15.1	15.7
Carbon monoxide	ppm	4	1

The concentration of each individual POHC in the waste feeds was kept relatively constant throughout the test. The concentration varied between POHC's from 2 to 25 percent, depending on the amount that was native to the waste. Sulfur hexafluoride was fed at a rate of 2 to 10 pounds per hour (lb/h) in the liquid waste feed line and 0.15 lb/h in the solid waste.

POHC INCINERABILITY RANKING

This section presents the data on POHC DRE's gathered during this study and an evaluation of the ranking of these DRE's compared to the ranking predicted by EPA's thermal stability ranking system. One of the seven POHC's selected for the study (methyl ethyl ketone) was present in the waste feeds at unexpectedly low concentrations; therefore, the following discussion addresses only the other six POHC's.

Table 3 shows the average DRE's for each of the two process operating conditions. These two conditions differed principally in that Condition A had combustion temperatures about 200°F higher than Condition B. The DRE data show little difference between these two conditions, with the possible exception of methylene chloride. Methylene chloride DRE's appeared to be slightly higher for Condition A. In general, daily averages differed as much as the condition averages, and the differences were within expected sampling and analysis accuracy. Because these differences between the conditions were

small and appeared random, data for both conditions were combined for the evaluation of the ranking discussed below.

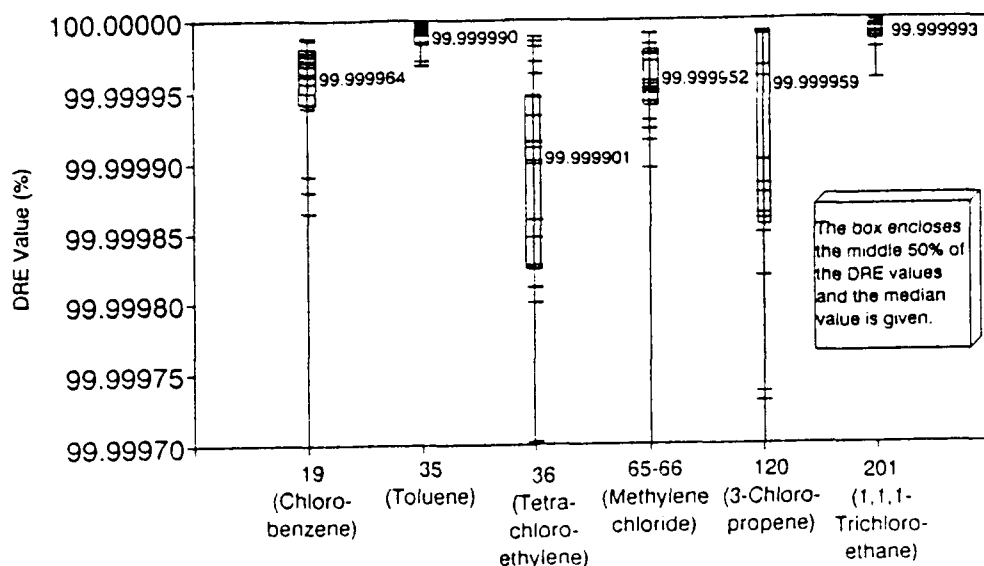
TABLE 3. AVERAGE POHC DRE's

POHC	Average DRE, percent	
	Test Condition A	Test Condition B
Chlorobenzene	99.999955	99.999923
3-Chloropropene	99.99984	99.999904
Methylene chloride	99.999969	99.99990
Tetrachloroethene	99.99988	99.99986
Toluene	99.999985	99.999991
1,1,1-Trichloroethane	99.999991	99.999991

Figure 2 displays the DRE results compared to the predicted thermal stability ranking. The measured DRE's are shown on the figure as the range of individual sample values, the middle 50 percent of the values (boxes on the figure), and the median values for each POHC. The data are arrayed on the figure by POHC with data for the hardest-to-destroy POHC to the left, increasing to easier-to-destroy POHC's to the right. The thermal stability/incinerability index is shown at the bottom of the figure. If the ranking of the measured DRE's matched the ranking predicted by the thermal stability index, the DRE's should increase from POHC to POHC from left to right on the figure.

Considering only the median value for each POHC, four of the six POHC's ranked correctly relative to one another. The two that did not rank as predicted, chlorobenzene and toluene, were easier to destroy than predicted. Considerable overlap occurs, however, in the ranges of values for each POHC. This data scatter is greater than typically observed for VOST trial burn results for two reasons. First, each data point is the analytical result for a single pair of traps, while trial burn results are expressed as an average of several pairs of traps. This averaging reduces the apparent scatter in the data. Second, the results of the SIM analysis had more scatter than typical VOST analysis results because of the extremely low levels that were quantified.

The measured DRE values were subjected to nonparametric (rank order) statistical tests for further evaluation. The statistical tests showed a high degree of consistency in the measured ranking from sample to sample throughout the test. They also confirmed the discussion above relative to the agreement with the predicted ranking.



Thermal Stability Incinerability Index

Figure 2. DRE for each POHC.

Two factors that related to how the data were reduced were investigated to determine if they affected the observed ranking of the POHC's. These factors were blank correction of the data and the relationship between POHC concentration in the waste and DRE. Blank corrections are discussed first below.

Because of the low levels of detection achieved with the SIM analysis, blank trap levels were a problem for some compounds, most noticeably for toluene, 3-chloropropene, and 1,1,1-trichloroethane. When blank levels are significant, they bias the concentration and emission rates high and the DRE's low. To check the effect on ranking of the calculated DRE's, a simple subtraction of blank levels was used to correct the data. Figure 3 shows the unadjusted and blank-corrected DRE's. Blank correction increased all the DRE's, but the ranking trend did not change.

Figure 3 also shows the feedrate-normalized DRE's. An earlier study identified the effect of POHC concentration in the waste feed on measured DRE's. Destruction and removal efficiency increases as the POHC concentration increases. A similar relationship was found using the data from this study, which was used to calculate the feedrate-normalized DRE's plotted in Figure 3. This correction of the calculated DRE's increased some values, decreased others, and did not change others. However, as happened for the blank-corrected DRE's, the ranking trend did not change.

Figure 3 also shows DRE's calculated considering both of the above corrections together. Again, the ranking trend is the same. The effect of these corrections, however, was to decrease the differences in DRE from POHC to POHC. The lowest and highest corrected DRE's differed by a factor of only 20.



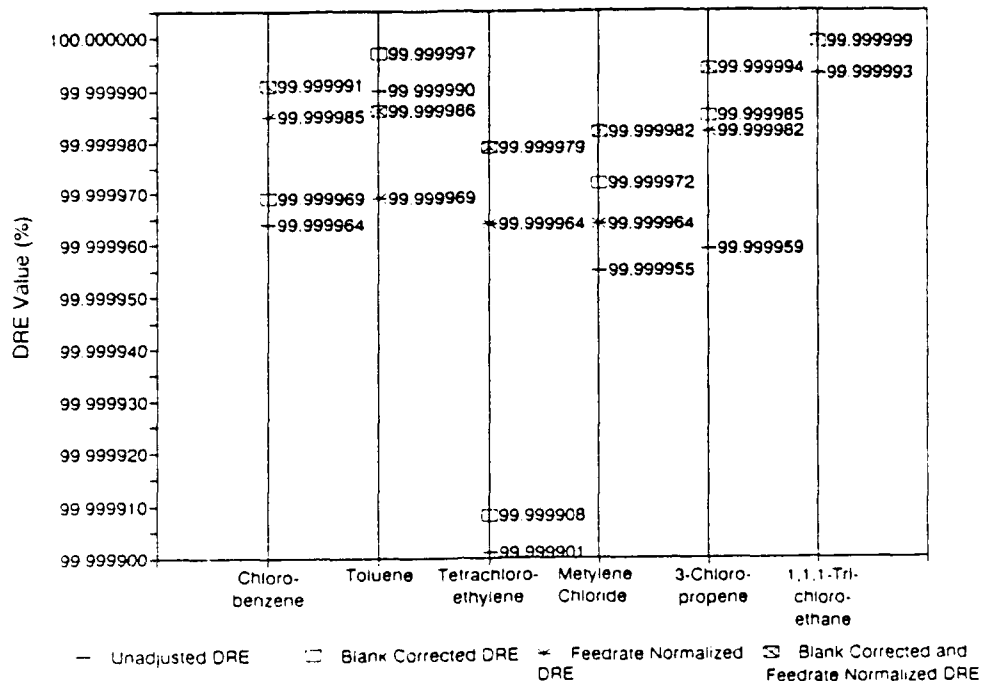


Figure 3. Comparison of corrected DRE values.

SF₆ DESTRUCTION

The study objective related to SF₆ focused on two questions about the use of this compound as a surrogate compound to measure POHC DRE. The first question concerned the effect on SF₆ DRE of the method of introducing the SF₆ to the incinerator. Conceivably, the method of introduction could affect what combustion conditions the SF₆ experiences. Historically, studies of SF₆ as a surrogate compound have introduced the SF₆ by spiking it into the liquid waste line or combining it with the combustion air. No study was identified where SF₆ was introduced with solid waste.

During one day of the test, SF₆ was spiked alternately into the solid and liquid waste streams. For the first half of the day, SF₆ was spiked as a gas into the liquid waste feed line. During the second half of the day, the microencapsulated SF₆ was placed into the drums of solid waste to be fed to the incinerator. No other process parameters were changed on this day. The average DRE's measured when the SF₆ was fed with the liquid and solid wastes were 99.989 and 99.986 percent, respectively. Thus, the method of feeding SF₆ into the incinerator via liquid or solid waste to the kiln did not affect the DRE.

The second question was whether SF₆ gives a conservative value of DRE relative to the POHC DRE's. Earlier studies have generally shown that SF₆ DRE is conservative (has a lower DRE) relative to POHC DRE's. Figures 4 and 5 show that the data from this study confirm the earlier studies. Figure 4 shows that the SF₆ DRE during Condition A (the higher-combustion-temperature condition, where the highest SF₆ DRE's were measured) was an order of

magnitude or more lower than the POHC DRE's. Figure 5 shows the same result during Condition B, but the SF₆ DRE's were even more conservative.

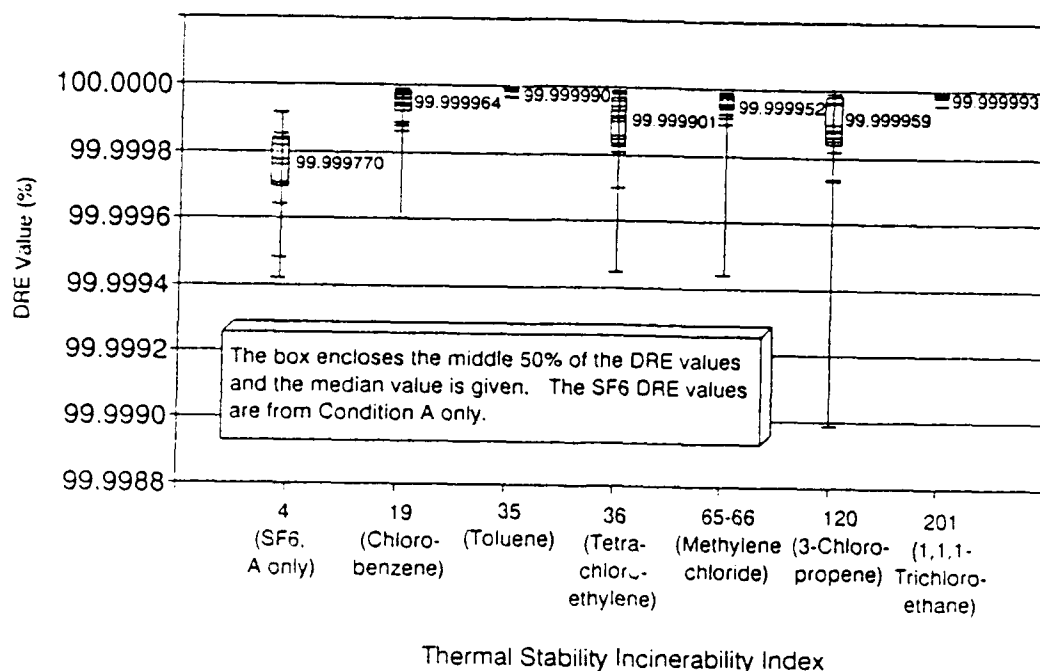


Figure 4. SF₆ and POHC DRE values.

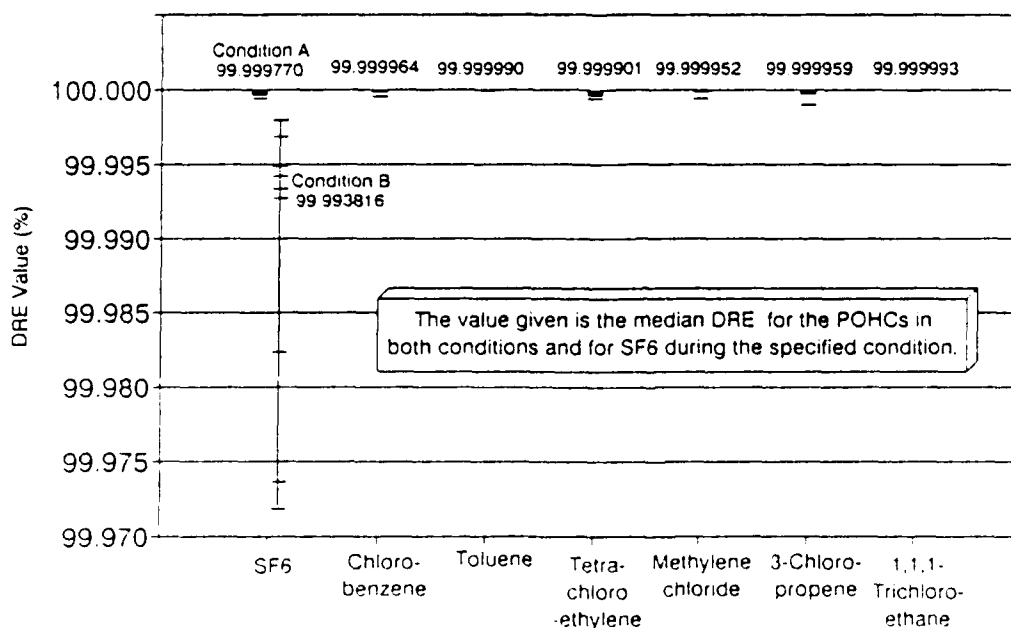


Figure 5. SF₆ and POHC DRE values.



As can be seen on Figure 5, the SF_6 DRE's measured during Condition B were considerably lower than the SF_6 DRE's measured during Condition A. These data indicate a dependence of SF_6 DRE on combustion temperature. Combustion temperatures during Condition A were 1730°F and 1920°F in the kiln and secondary chamber, respectively. During Condition B, they were 1510°F and 1700°F, respectively. Thus, the SF_6 DRE decreased from 99.9998 to 99.994 percent, with a 200°F drop in combustion temperature. Earlier discussions showed that a similar dependence on combustion temperature was not observed for the POHC's. As a result, SF_6 becomes a more conservative indicator as combustion temperature decreases.

CONCLUSIONS

Below are brief statements of the primary conclusions from this study.

1. The DRE for POHC's ranked highest by the thermal stability ranking system (those easiest to destroy) generally followed the ranking order predicted by the system.
2. The DRE's for the two POHC's studied that were ranked lowest by the system (chlorobenzene and toluene) did not agree with the predicted ranking order. They were easier to destroy than predicted.
3. The 200°F change in combustion temperature between test conditions did not affect the POHC DRE's or the observed ranking order.
4. The measured ranking order was very consistent from test period to test period (sample to sample).
5. The DRE measured for SF_6 was lower than the DRE's for all the POHC's studied in this project; thus, SF_6 was a conservative indicator of POHC DRE.
6. The DRE for SF_6 had a distinct dependence on combustion temperature. A decrease in temperature of about 200°F caused a decrease in SF_6 DRE of about one order of magnitude.
7. The method of feeding SF_6 to the incinerator (in the liquid waste versus solid waste feed to the kiln) did not affect the DRE.

THERMAL TREATMENT OF WASTES IN AN ADVANCED CYCLONIC COMBUSTOR

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ABSTRACT

IGT is developing an advanced waste combustion concept, based on cyclonic combustion principles, for application to a wide range of industrial wastes. In IGT's cyclonic combustor, a mixture of fuel and combustion air is fed tangentially at a relatively high velocity into a cylindrical chamber. The waste is injected either tangentially with the fuel or separately in a tangential, radial, or axial configuration. This approach provides high combustion intensity with internal recirculation of combustion products, which results in extremely stable and complete combustion, even at relatively low temperatures.

Compared with other types of waste combustors, the cyclonic unit offers several important advantages: better mixing and temperature uniformity, higher destruction and removal efficiency (DRE), a wider operating range, greater flexibility to variations in waste properties, molten-ash discharge capability, and more efficient heat recovery at reduced capital and operating costs.

IGT has performed three successful test programs involving cyclonic waste combustion for industrial clients. In one program, industrial wastewaters containing 40% to 50% organics and inorganics with heating values of 1600 to 3270 Btu/lb were combusted to 99.9% completion at only 2000°F. The low combustion temperature minimized the supplemental fuel required. In another program, simulated low-Btu industrial off-gases (55 to 65 Btu/SCF) were successfully combusted with stable combustion at 1900°F using air and waste preheat. Supplemental fuel was unnecessary because of the mixing that occurs in the cyclonic combustor. The conversion of fuel-bound nitrogen to NO_x was as low as 5%, and CO levels were in the range of 25 to 30 ppm. In the third program, CCl_4 (as a test surrogate for PCBs) was efficiently destroyed by firing natural gas or hexane. With 100% CCl_4 and natural gas firing, the DRE at 2200°F and a 0.25-second residence time ranged from 99.9999% to 99.99999%.

These successful tests have led to the design and construction of a modular test facility at IGT's Energy Development Center. The 1 to 3 million Btu/h facility uses an improved,



second-generation cyclonic waste combustor and is complete with gaseous, liquid, and solid fuel feeding systems as well as downstream gas conditioning equipment. It also includes a cold-flow aerodynamic model capable of studying both liquid and gaseous fluids.

IGT is currently using this facility to develop a slagging cyclonic combustor for a class of industrial solid wastes. The first waste being evaluated is a spent aluminum potliner product. The process is being designed to produce a molten (i.e., benign) ash while emitting a flue gas stream that contains less than 25 ppm carbon monoxide and total hydrocarbons.

INTRODUCTION

The U.S. Federal Government responded to the critical waste problem with the enactment of the Resource Conservation and Recovery Act (RCRA) in 1976, the Toxic Substance Control Act (TSCA) in 1976, the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) in 1980, the RCRA Amendment of 1984, and the most recent Superfund Amendments and Reauthorization Act of 1986 (SARA) to ensure the reliable management of hazardous toxic waste disposal operations and dump site cleanup. The enactment of these laws has intensified interest in the thermal destruction of organic/inorganic wastes.

Thermal treatment of wastes has long been recognized as one of the best demonstrated and available technologies for waste disposal. It is an engineered process, with waste destruction being the ultimate goal. Its function is to use heat to break the chemical structures of organic compounds, thus reducing the volume and toxicity of the residuals.

Thermal treatment of wastes (hazardous and nonhazardous) continues to be strongly favored in the U.S. and abroad as one of the best alternatives to landfilling. Many observers expect that this mode of waste disposal will become more firmly established as a means of minimizing landfilling in the U.S.; this has certainly been the case in Europe and Japan. The benefits of thermal treatment over other disposal methods are even more pronounced in the U.S. with relatively low fuel prices. Hence, there is an enormous potential for more capacity to be built over the next 2 to 10 years.

Commercially available technologies for the thermal treatment of hazardous and nonhazardous liquid, gaseous, and solid wastes use a variety of methods that include combustion chambers with low swirl, rotary kilns, multiple hearths, and moving grates.

Significant technological advances have been made during the past few decades; however, these common technologies still suffer from a variety of drawbacks:



- High excess combustion air requirement to achieve high DRE
- Low combustion intensity
- Inability to efficiently separate ash from combustion products in the combustion chamber
- Inability to maintain stable, continuous operation
- Short refractory life when molten ash is present in the products of combustion
- Low thermal efficiency of heat recovery equipment
- High capital cost because of relatively large combustion chamber and/or design complexity
- High operating cost because of high auxiliary fuel usage.

There is a need, therefore, for advanced thermal treatment technologies that can overcome these drawbacks. One such advanced technology, under development at IGT for the past few years, is based on the cyclonic combustion concept. As illustrated in Figure 1, it involves the injection of a mixture of auxiliary fuel (natural gas) and combustion air at a relatively high velocity into a cylindrical combustion chamber. The waste is injected either tangentially with the auxiliary fuel or separately in a tangential, radial, or axial configuration. This approach provides high combustion intensity with internal recirculation of combustion products, which results in extremely stable and complete combustion, even at relatively low temperatures. Compared with other types of waste combustors, the cyclonic unit offers several important advantages:

- Lower excess air requirement
- Higher combustion intensity
- Lower supplementary fuel requirement
- Better mixing and temperature uniformity
- Wider operating range
- Greater flexibility to variations in waste properties
- Dry ash or molten (vitrified) ash discharge
- Longer refractory life
- Higher efficiency of heat recovery equipment
- Lower capital and operating costs.



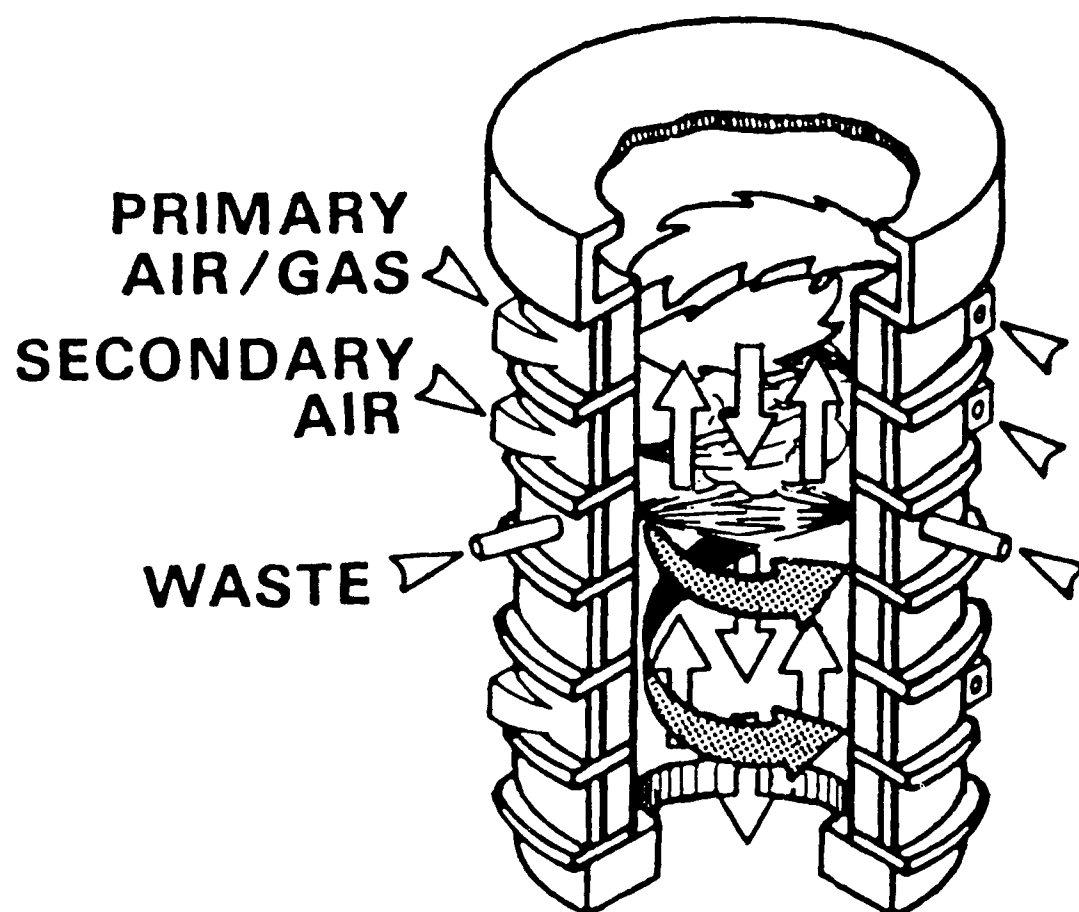


Figure 1. TANGENTIAL SWIRL AND INTERNAL RECIRCULATION PATTERNS

IGT has performed three test programs involving cyclonic combustion for industrial clients. In one program with a pilot-scale unit, several industrial wastewaters containing 39% to 50% organics and inorganics were treated at a rate of 1×10^6 Btu/h. The wastewaters, with heating values of 1600 to 3270 Btu/lb, were combusted in the dry ash mode at combustion temperatures of 2000°F using natural gas as the supplementary fuel. The major results can be summarized as follows:

- For a selected wastewater, stable operation was demonstrated for 48 continuous hours.
- High combustion intensity (0.25×10^6 Btu/h-ft³) and excellent combustion completion (>99.9%) were achieved.
- Excess combustion air levels ranged from 10% to 25%.
- Ash accumulation on the combustor and exhaust duct surfaces was relatively low.
- The combustor chamber refractory lining performed well with no observed damage.

Subsequently, one of the wastewaters was treated on-site in a 3×10^6 Btu/h demonstration system. Another wastewater was successfully treated in the slagging mode with molten ash discharge by premixing it with 5% glass cullet to reduce the ash fusion temperature.

In another program, IGT treated a simulated low-Btu industrial off-gas (55 to 65 Btu/SCF) with stable combustion at 1900°F using air and waste preheat. The gas contained H₂, CO, CH₄, and NH₃. The test unit was operated at a rate of 3×10^6 Btu/h. Supplemental fuel was unnecessary because of the mixing that occurs in the cyclonic waste combustor. The conversion of NH₃ to NO_x was as low as 5%, and CO levels were in the range of 25 to 30 ppm. The NO_x level with no NH₃ added was below 10 ppm.

For the third program, CCl₄ (as a test surrogate for PCBs) was efficiently destroyed by firing natural gas or hexane at an approximate rate of 1×10^6 Btu/h. With 100% CCl₄ and natural gas firing, the DRE at 2200°F and a 0.25-second residence time ranged from 99.9999% to 99.99999%. The CCl₄ remaining in the combustion products was at the parts-per-trillion levels.

These successful tests led to the design and construction of a cyclonic waste combustion modular test facility at IGT's Energy Development Center. It is currently being configured to evaluate the treatment of spent aluminum potliners, to produce benign vitrified ash. This paper describes the test programs that have been undertaken on the cyclonic waste combustor, describes the modular cyclonic waste combustion test facility, and discusses the current program to treat SPL.



PILOT-SCALE CYCLONIC COMBUSTION OF LIQUID WASTES

The original pilot-scale system, as illustrated in Figure 2, consisted of the following major components:

- Highly flexible cyclonic waste combustor
- Waste storage and supply subsystem
- Combustion air and natural gas subsystem
- Atomizer assembly
- Cooling water subsystem
- Compressed air subsystem
- Drum heating subsystem.

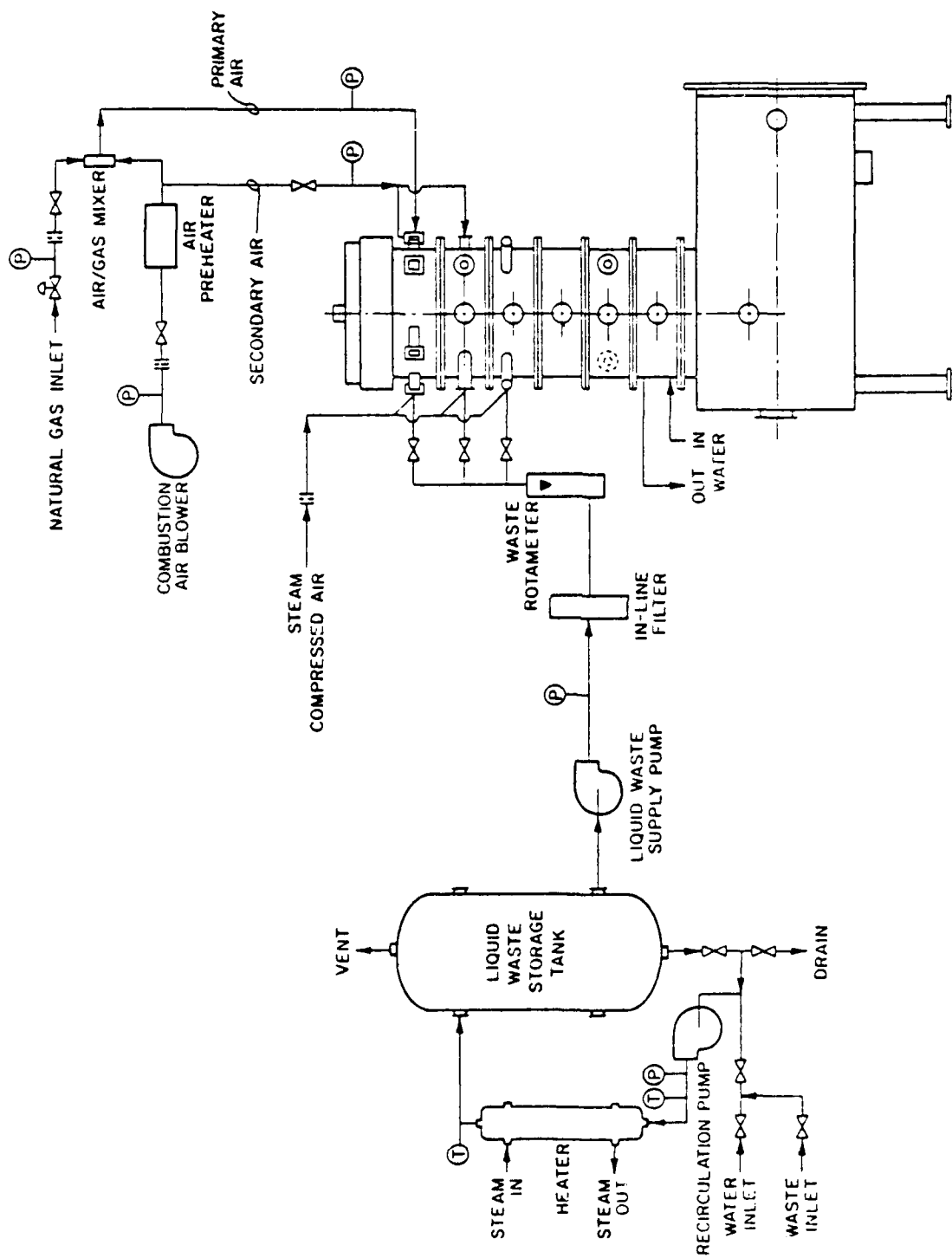
The cyclonic waste combustor was designed for a nominal firing rate of 3×10^6 Btu/h and consisted of interchangeable cylindrical sections atop a base section that served as an ash/slag receiver. Each cyclonic chamber section incorporated a water-cooled annulus and an interior refractory lining. The approximate height and diameter of the combustor unit were 3.50 and 2 feet, respectively.

The key section in the combustion chamber was located at the top of the chamber; it contained six evenly spaced tangential nozzles through which primary combustion air (preheated up to 800°F), natural gas, and waste might enter the chamber. Primary combustion air and natural gas were mixed prior to entering the tangential nozzles while the liquid waste and compressed air were introduced using injectors positioned inside and along the axis of the tangential nozzles.

A second important chamber section was the refractory orifice section located at the bottom of the incineration chamber immediately above the base. The orifice had a smaller inside diameter than the major portion of the chamber, which enhanced the cyclone swirl and promoted the recirculation of combustion products to the top of the cyclonic chamber.

Other sections of the chamber served various purposes. Beneath the section containing the six tangential nozzles was a section featuring four tangential nozzles for the introduction of secondary combustion air (also preheated up to 800°F) or waste or both. Below this was a section containing four radial nozzles through which waste could enter the chamber. The remaining sections of the chamber served to satisfy the height-to-diameter ratio required for satisfactory combustion of the waste.





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Figure 2. SIMPLIFIED SCHEMATIC DIAGRAM OF THE IGT PILOT-SCALE CYCLONIC WASTE COMBUSTION SYSTEM



Except for the top nozzle section, all sections of the cyclonic combustor unit, including the base, incorporated openings for the gathering of data or viewing of the incinerator interior. These openings allow entry of water-cooled probes for composition sampling or temperature measurements of combustion products.

The waste combustion chamber was designed so that molten slag will freeze on the refractory lining because of the cooling effect of the water, thereby protecting the refractory from both the erosive and corrosive actions of high-velocity molten slag.

The key components in the design of the combustor were the geometry, nozzle orientation, injection technique, and injector type used to introduce the liquid waste into the combustion chamber.

Tests With Industrial Wastewater No. 1

Waste Characteristics

The typical wastewater used in the tests contained about 50% dissolved solids and had a higher heating value (HHV) of approximately 3270 Btu/lb. The chemical composition of one of the "as-received" dewatered waste samples is shown in Table 1; the fusion characteristics of the inorganics in the wastewater are presented in Table 2. The ashing temperatures are temperatures used to "burn out" the organic material in the dewatered sample.

The data show that the ash fluid temperature is approximately 2750° to 2800°F, regardless of the ashing temperature. In addition, the fluid temperatures are very similar for both oxidizing and reducing conditions.

The chemical composition of the 1000° and 1900°F ash samples is shown in Table 3. The 1900°F ash sample was analyzed for chloride content and contained less than 0.01% chloride by weight (dry basis).

Table 1. PROXIMATE/ULTIMATE ANALYSIS OF DEWATERED WASTE

<u>Proximate Analysis</u>		<u>Ultimate Analysis</u>	
	<u>wt. %</u>		<u>wt. %</u>
			(Dry Basis)
Moisture	0.88	Ash	4.7
Ash	4.66	Carbon (Total)	37.45
		Hydrogen	6.28
		Sulfur	0.14
		Nitrogen	0.76
		Oxygen (by Difference)	50.67
		Total	100.00



Table 2. SUMMARY OF FUSION TEMPERATURE OF ASH

Ashing Temperature, °F	1000	1300	1600	1900
Oxidizing Atmosphere, °F				
Initial Deformation	1730	1720	2360	2385
Softening	2585	2590	2550	2770
Hemispherical	2730	2715	2765	2790
Fluid	2740	2745	2795	2800
Reducing Atmosphere, °F				
Initial Deformation	1780	1870	2505	2490
Softening	2695	2710	2690	2695
Hemispherical	2725	2735	2735	2720
Fluid	2750	2755	2775	2785

Table 3. CHEMICAL COMPOSITION OF ASH

<u>Composition</u>	<u>Sample Ashed at 1000°F</u>	<u>Sample Ashed at 1900°F</u>
SiO ₂	0.48	0.41
Al ₂ O ₃	0.11	0.13
Fe ₂ O ₃	0.06	0.14
TiO ₂	0.09	0.09
P ₂ O ₅	18.45	33.66
CaO	9.74	22.90
MgO	2.48	5.0
Na ₂ O	11.41	14.61
K ₂ O	27.21	16.00
SO ₃	6.3	7.5
Totals	76.3	100.4



Dry Ash Test Results

Some of the performance test results are shown in Table 4. The data indicate that stable and complete combustion was achieved. The waste/natural gas heat contribution ratio was 59:41 for Test No. 1 and 63:37 for Test No. 2.

Following the performance tests, a final 48-hour continuous test was conducted. For this test, however, the waste used contained approximately 35% solids.

During the 48-hour test, data were collected approximately every hour; some results are shown in Table 5. As expected, the data indicate a higher natural gas consumption than in previous tests. The average waste/gas heat contribution ratio was 41:59. About 25% of the total heat input was removed by the cooling water. Most of this heat would be usable in a commercial system, which would either not use any cooling water or employ a heat recovery boiler. Test Nos. 36 through 41 were performed at a turndown ratio of 1.6:1 (35% below normal operation) and reduced combustion temperature (1900°F).

A total of 750 gallons of wastewater was treated during the 48-hour test. There were no shutdowns, and the operation was generally free of difficulties.

The major results of the pilot-scale tests can be summarized as follows:

- Stable operation was demonstrated for 48 continuous hours using a feed rate of approximately 15 gallons per hour.
- The optimum ratio of waste heat input to natural gas heat input was approximately 60:40 (for 50% solids concentration), producing a total firing rate of approximately 0.8×10^6 Btu/h.
- High combustion intensity (0.25×10^6 Btu/h-ft³) and excellent combustion efficiency (>99.9%) were achieved.
- Excess combustion air levels ranged from 10% to 25%.
- The ability to combust wastewaters of various concentrations was demonstrated (varied from roughly 35% to 55% solids).
- Ash accumulation was relatively low on the combustor walls, orifice, base, and exhaust duct.
- The combustion chamber refractory lining performed well with no observed damage.

Slagging Test Results

It had been proven (using laboratory samples) that it is possible to lower the fusion temperatures of the ash by using additives that do not interfere with the pumping and combustion characteristics of the wastewater. Lowering the fusion temperatures allows the



Table 4. RESULTS FOR INDUSTRIAL WASTEWATER NO. 1

Test No.	Natural Gas Firing Rate, 10 ⁶ Btu/h	Primary Air/Natural Gas Mixture Temperature, °F	Secondary Air Temperature, °F	Exhaust Gas Analysis		Base/Slag Receiver Wall Temperature, °F
				O ₂ , %	CO, ppm	
1	0.34	490	728	2.1	150	1745
2	0.33	439	745	2.1	40	1820

Table 5. SYSTEM OPERATING PARAMETERS DURING 48-HOUR PERFORMANCE TEST

Test No.	Natural Gas Firing Rate, 10 ⁶ Btu/h	Primary Air/Natural Gas Mixture Temperature, °F	Liquid Waste Flow, gal/h	Secondary Air Temperature, °F	Exhaust Gas Analysis O ₂ , %	CO, ppm	CO ₂ , %	Base/Slag Receiver Wall Temperature, °F
1	0.465	477	15.7	725	2.3	50	--	2010
5	0.475	485	15.7	727	2.2	50	--	2085
12	0.48	477	13.5	727	2.9	50	13.0	2093
16	0.48	480	14.8	726	3.2	150	13.25	2111
21	0.49	478	13.9	724	2.6	50	13.5	2098
25	0.45	467	13.9	724	2.4	75	13.5	2086
27	0.455	464	13.9	723	2.2	50	12.75	2095
36	0.32	392	8.7	694	4.8	275	10.75	1818
41	0.35	347	8.7	682	4.3	100	10.75	1886
44	0.30	384	13.9	700	3.0	150	13.25	2072

combustor to operate in a slagging mode at lower temperatures and with lower natural gas consumption. The two additives, microfine glass cullet (99.9% minus 325 mesh) and Apex 700 powder, had been examined by IGT's Analytical Laboratory (Table 6) and were found to lower the initial deformation temperatures by 750° and 100°F and the fluid temperatures by 400° and 300°F, respectively. The glass cullet, which showed a higher temperature reduction, was selected for testing on the pilot unit.

Table 6. ASH FUSION TEMPERATURE CHARACTERISTICS
IN ADDITIVE/WASTE MIXTURE

	<u>Microfine Glass Cullet</u>	<u>Apex 700 Powder</u>
Oxidizing Atmosphere, °F		
Initial Deformation	1610	2260
Softening	2030	2390
Hemispherical	2250	2410
Fluid	2420	2520
Reducing Atmosphere, °F		
Initial Deformation	1560	2230
Softening	1860	2380
Hemispherical	2240	2400
Fluid	2370	2510

The unit was preheated to about 2300°F using natural gas before wastewater was injected. When stable operation was achieved, the microfine glass cullet was slowly added into the preheated (160°F) waste tank. A total of 26.2 lb of glass cullet was mixed into a barrel containing approximately 510 lb of waste. The data collected during the test run are shown in Table 7.

The operation of the combustor throughout the testing was stable and without any difficulties. The formation and presence of slag on the interior surfaces of the combustor could not be observed during operation. After the unit was cooled, however, the following was observed:

- A thin layer of the frozen slag was present on the walls and orifice of the combustion chamber and floor of the slag receiver.
- The slag covered the entire wall surface of the combustor, starting at the level of the waste injection and progressing to the orifice at the bottom of the combustor.

The average waste/gas heat contribution ratio during these tests was 13:87 and the glass cullet/liquid waste ratio was 5:95 (on weight basis).



Table 7. RESULTS FOR MIXTURE OF WASTEWATER AND GLASS CULLET

Test No.	Natural Gas Firing Rate, 10 ⁶ Btu/h	Primary Air/Natural Gas Mixture Temperature, °F	Liquid Waste Flow, gal/h	Exhaust Gas Analysis			Base/Slag Receiver Wall Temperature, °F
				O ₂ , %	CO, ppm	CO ₂ , %	
1	1.06	621	3.8	1.4	90	12.0	2305
2	1.06	623	3.9	1.1	95	12.0	2344
3	1.06	626	3.9	1.7	60	11.3	2318
4	1.06	--	4.4	1.5	75	11.5	2369
5	1.06	--	4.4	1.3	90	11.5	2383
6	1.06	628	4.4	0.7	105	11.5	2395
7	1.06	628	4.1	0.8	110	12.3	2395
8	1.06	628	4.0	1.3	80	11.5	2382

Tests With Industrial Wastewater No. 2

Waste Characteristics

Wastewater No. 2 contained approximately 61% water, 26.5% dissolved organics (HHV about 6000 Btu/lb), and 12.5% dissolved inorganics. Its HHV (wet, as tested) was about 1600 Btu/lb.

During the mixing and preheating of the waste, it was found that the waste thickens or coagulates when heated. After some sample tests in the laboratory, it was decided not to preheat the waste.

Test Results

The performance test results with this waste are presented in Table 8. During the tests, the unit operated without any difficulties. The combustion was stable, and no unburned liquid waste was observed on the combustor walls. The flow of wastewater into the combustor was stable, and the waste atomizers did not show any signs of overheating. The flame inside the combustor was observed to be very luminous and stable.

The major results can be summarized as follows:

- The wastewater was effectively and completely combusted.
- Low excess air (10% to 15%) operation was achievable and sustainable.

Tests With Industrial Wastewater No. 3

Waste Characteristics

The dry waste sample was analyzed for chemical composition as well as for ashing/fusion temperature characteristics. Wastewater No. 3 contained 56% water. The HHV of its organics content was 7200 Btu/lb and of the waste as tested was 2600 Btu/lb. The fusion tests were conducted in an oxidizing atmosphere for 1000°F and oxidizing and reducing atmosphere for 1600° and 1900°F. The results, presented in Table 9, show that the fluid temperature of the ash is approximately 2640° to 2740°F, regardless of the ashing temperature and atmosphere in which the fusion takes place; however, the ash percent in the sample does vary with the ashing temperature. At 1000°F ashing temperature, the amount of ash was found to be 16.5%; at 1900°F ashing temperature, the amount of ash dropped to only 6.0%.



Table 8. RESULTS FOR INDUSTRIAL WASTEWATER NO. 2

Test No.	Natural Gas Firing Rate, 10 ⁶ Btu/h	Primary Air/Natural Gas Mixture Temperature, °F	Liquid Waste Flow, gal/h	Exhaust Gas Analysis			Base/Slag Receiver Wall Temperature, °F
				O ₂ , %	CO, ppm	CO ₂ , %	
1	.05	385	2.6	2.2	60	10.0	1240
2	.06	400	10.9	4.4	70	8.0	1595
3	.06	400	12.5	3.0	45	--	1736
4	.06	400	12.5	2.9	140	10.0	1845

Table 9. SUMMARY OF FUSION TEMPERATURE OF ASH

Ashing Temperature, °F	1000	1600	1900
Oxidizing Atmosphere, °F			
Initial Deformation	1660	2550	2590
Softening	2020	2570	2610
Hemispherical	2580	2620	2630
Fluid	2640	2680	2700
Reducing Atmosphere, °F			
Initial Deformation		2630	2660
Softening		2700	2710
Hemispherical		2710	2720
Fluid		2730	2740
Ash Content, %	16.5		6.0

The ashes with an ashing temperature at 1000° and 1900°F were analyzed for chemical composition. For a better understanding of the variations in percentage of ashes at 1000° and 1900°F ashing temperature, the chemical constituents found in the ashes were recalculated to the original sample bases. The results, presented in Tables 10 and 11, show that the NaCl and KCl evaporated, lowering the amount of ash from 16.5% at 1000°F to 6% at 1900°F.

Test Results

Table 12 presents the results of tests with industrial wastewater No. 3. The unit operated without any difficulties. Combustion was stable and complete. The flow of the waste into the combustor was stable as well, and the waste atomizers did not show any signs of overheating. The flame inside the combustor was very luminous and appeared to be stable. The average waste/gas heat contribution ratio during these tests was 30:70.

After completion of the testing, the interior of the chamber was inspected. The following observations were made:

- A thin layer of powdery, golden-colored ash covered the walls of the combustor and hearth of the base.
- No ash deposition was found on the top portion of the chamber walls at the level of the primary combustion air/natural gas nozzles.
- The chamber wall area downstream of the atomizer level was relatively clean, with ash deposits evenly distributed around the chamber.



Table 10. CHEMICAL COMPOSITION OF ASH

<u>Composition</u>	<u>Sample Ashed at 1000°F</u>	<u>Sample Ashed at 1900°F</u>
SiO ₂	0.17	0.25
Al ₂ O ₃	0.05	0.05
Fe ₂ O ₃	0.05	0.10
TiO ₂	<0.09	<0.09
P ₂ O ₅	16.10	41.29
CaO	6.37	18.68
MgO	1.89	5.23
Na ₂ O	7.10	27.41
K ₂ O	--	2.50
SO ₃	1.8	4.43
NaCl	25.65	--
KCl	33.10	--

Table 11. CHEMICAL COMPOSITION OF ASH CALCULATED
TO ORIGINAL SAMPLE BASES

<u>Composition</u>	<u>Sample Ashed at 1000°F</u>	<u>Sample Ashed at 1900°F</u>
Si	0.013	0.007
Al	0.004	0.002
Fe	0.009	0.004
P	1.16	1.08
Ca	0.75	0.79
Mg	0.188	0.188
Na	2.53	1.21
K	2.86	0.13
Cl	5.16	0.001
F	0.008	0.006

Table 12. RESULTS FOR INDUSTRIAL WASTEWATER NO. 3

Test No.	Natural Gas Firing Rate, 10 ⁶ Btu/h	Primary Air/Natural Gas Mixture Temperature, °F	Secondary Air Temperature, °F	Liquid Waste Flow, gal/h	Exhaust Gas Analysis				Base/Slag Receiver Wall Temperature, °F
					O ₂ , %	CO, ppm	CO ₂ , %	NO _x , ppm	
1	0.7	289	377	12.6	3.6	25	13.3	300	2084
2	0.8	286	372	13.5	3.6	35	12.8	3 ^a	2110
3	0.8	285	371	10.9	3.4	195	12.8	--	2133
4	0.8	290	372	15.9	2.6	105	13.8	--	2188

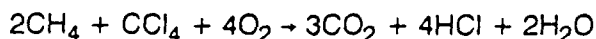
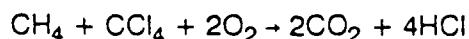
Tests With Carbon Tetrachloride

Carbon tetrachloride (CCl_4) was selected as the surrogate material for testing the polychlorinated biphenyl (PCBs) treatment capability. CCl_4 is generally believed to be more stable than PCBs, is relatively nontoxic, and will not result in products of incomplete combustion (PICs) that are highly toxic.

To determine carbon tetrachloride's DRE, high-temperature gas samples were drawn from the combustion system, through a modified EPA Method 5 analytical train, and the residual CCl_4 was trapped in double Tenax beds in series. Sample volumes of 20 liters were drawn and measured by a meter that was calibrated and temperature-compensated. Double tubes of absorbent were used in the traps to assure complete recovery; a system of blanks and sample spikes was used to verify the analytical technique.

The sample traps were analyzed by gas chromatography/mass spectrometry (GC/MS) techniques. This approach was shown to have a sensitivity of about 0.7 micrograms of CCl_4 in the sample (0.9 micrograms sensitivity was used for data reduction). The sensitivity was sufficient to measure six-9's destruction efficiency.

The destruction of CCl_4 in a methane-fueled combustor requires no additional oxygen. The chemistry at two stoichiometric ratios of CCl_4/CH_4 is as follows:



The heat effect of the CCl_4 is nearly negligible. Specifically, at a CCl_4/CH_4 ratio of 0.5, the heat of reaction is essentially identical to the heat of combustion of methane alone.

The system incorporated scrubbing, with neutralization of the spent scrub liquor, and an ID fan to maintain a slight vacuum in the combustion chamber.

The tabulated results of the tests are summarized in Table 13.

In most of the tests, the unit was operated with an 800°F* combustion air preheat and a gas firing rate of about 0.8×10^6 Btu/h. The gas sampling probe was located immediately beneath the cyclonic combustion chamber, with a hot gas residence time of approximately 0.25 seconds. Temperatures were measured by a suction pyrometer near the exhaust of the combustor base, after a gas residence time of about 0.75 second.

* This degree of air preheat approximately counteracts the combustor cooling attributable to the cooling water. In the production unit, it is anticipated that this water cooling would not be required, and the preheat was used to account for this effect.

Table 13. CCl₄ COMBUSTION TEST SUMMARY

Test No.	Firing Rate, 10 ⁶ Btu/h	NG/Air Temp., °F	Suction Pyrometer Base Temp., °F	Exhaust Gas Analysis				CCl ₄ Flow, lb/min.	CCl ₄ /NG Ratio	CCl ₄ Recovered, µg/20 L	Destruction Efficiency, %	Comments
				O ₂ , %	CO ₂ , %	CO, ppm	NO, ppm					
1	1.0	695	2338*	2.5	10.25	68	--	--	--	--	--	NG Only.
2	0.8	685	2098*	3.7	10.5	55	--	1.44	0.270	<0.9	99.99997	
6	0.8	715	2520	3.7	12.5	36	170	3.3	0.618	2.7	99.99996	
10	0.7	704	1950	1.2	12.0	21	498	0.83	0.178	<0.9	>99.99996	Caustic Injection in Incinerator.
14	0.8	712	2458**	3.6	10.5	60	--	1.05	0.190	1.8	99.99992	
16	0.8	693	2533**	0.7	13.5	398	134	2.15	0.393	1.8	99.99996	Caustic Injection in Base.
17	0.8	406	2408**	3.5	11.5	60	60	2.15	0.393	5.1	99.99988	

* Suction pyrometer downstream.

** Thermocouple data.

The initial test was run with natural gas combustion only, without injection of CCl_4 . A blank sample was taken for CCl_4 analysis through GC/MS as part of the data quality assurance program.

The second two samples were run at approximately a 0.3 and a 0.6 molar ratio of CCl_4 to CH_4 . At the lower carbon tetrachloride feed rate, the CCl_4 remaining was below the limits of detection; at the higher rate, the CCl_4 remaining was 1.8 microgram in the 20-liter gas sample. Both of these results indicate significantly better than six-9's destruction. Therefore, downstream sample ports for improved destruction as a function of time were unnecessary.

Operation at low excess air did not significantly impair the destruction efficiency, nor did variations in the location of the sampling probe, across the diameter of the orifice plate, cause a noticeable effect.

For the next series of tests, a 40% caustic solution was injected directly into the combustion chamber to neutralize the hydrochloric acid as it was formed. With this direct caustic injection, a liquid scrubber was not required. Rather, the exhaust was ducted directly to the refractory-lined stack. During operation, the stack had no objectionable odor of either acid or caustic.

Relatively low temperatures were recorded by suction pyrometer directly under the combustor orifice during this series. Test conditions employed lower CCl_4/CH_4 ratios (about 0.14 to 0.2) and relatively low excess air ratios (O_2 about 1.2% to 1.7%).

In the last series of tests, the caustic solution was injected into the base about 2-1/2 feet downstream from the point where the gas composition and temperature data were acquired. For this series of tests, the temperature was measured by a small bare-bead thermocouple.

The tests investigated impacts of variations in excess air utilization, CCl_4/CH_4 ratio, and combustion air preheat. Test 17, with lower combustion air preheat, showed slightly less than six-9's CCl_4 destruction.

The major results of the tests with carbon tetrachloride can be summarized as follows:

- Carbon tetrachloride was destroyed in the cyclonic combustor, generally at greater than six-9's removal – with air preheated to 700°F, exhaust temperatures of 2400° to 2500°F, and a residence time of 0.25 seconds.
- Emissions of NO_x were 130 to 330 ppm under these conditions. With reduced air preheat (450°F), NO_x emissions dropped to 60 ppm, but CCl_4 destruction was slightly impaired.



- Generally, the destruction efficiency was high, regardless of the excess air level, combustor exhaust temperature, or CCl_4/CH_4 ratio. No correlations with these parameters could be determined.
- The direct injection of alkali into the combustor or into a hot zone downstream of the combustor appears to hold promise for HCl removal but requires further development.

Tests With Hexane Mixed With Carbon Tetrachloride

No natural gas was used during these tests. The analytical technique called Volatile Organic Sampling Train (VOST) was used in these tests utilizing two sorbent tubes connected in series. The sorbent tubes were thermally desorbed, and the content was analyzed by GC/MS technique. The approach was shown to have a sensitivity of 1 nanogram of CCl_4 per sample (20 liters). The sensitivity was sufficient to measure six-9's destruction efficiency.

Selected test results with 0.5% CCl_4 in hexane are presented in Table 14 and with 1% CCl_4 in hexane in Table 15. In most of the tests, the gas sampling probe was located beneath the combustor orifice, with a hot residence time of approximately 0.25 seconds.

The major results of the tests with this waste can be summarized as follows:

- Combustion efficiency of hexane was very high (CO not detectable) even at a low excess air level of about 10%.
- Carbon tetrachloride was destroyed, generally at greater than five-9's DRE, with combustion air preheated to 400°F, at exhaust temperatures of 2100° to 2200°F and a residence time of 0.25 seconds.
- NO_x emissions were relatively low under these conditions (90 to 130 ppm). With ambient combustion air, NO_x emissions dropped to 70 ppm.
- Generally, the DRE was high regardless of the excess air ratio and CCl_4 concentration in the hexane. Reduced air preheat had a slightly negative effect on the CCl_4 DRE.

LOW-BTU OFF-GAS TESTING

The combustion characteristics of low-Btu off-gases (from shale gasification) and the operating performance of a horizontal cyclonic combustor were tested to evaluate emissions and heat recovery potential. The basic flow diagram for the tests is shown in Figure 3, and the combustor setup is shown in Figure 4. Table 16 shows the composition of the low-Btu off-gases tested. The 54 Btu/SCF off-gas composition represents the minimum heating value expected, and the 67 Btu/SCF represents the average of the minimum and maximum heating value. It was also anticipated that the off-gas would contain up to 0.56% NH_3 and 0.15% H_2S .

Table 14. RESULTS FOR HEXANE MIXED WITH 0.5% CCl₄
(by Weight)

Test No.	Firing Rate, 10 ⁶ Btu/h	Thermocouple Base Temp., °F	Exhaust Gas Analysis				CCl ₄ Flow Rate, lb/h	CCl ₄ Recovered, 10 ⁻⁹ μg/20 L	Destruction Efficiency, %
			as Measured		at 0% O ₂				
			O ₂ , %	CO ₂ , %	CO, ppm	NO/NO _x , ppm			
1*	1.0	1808	3.0	11.50	0	64/64	--	250	--
2	1.0	1862	4.1	11.00	0	55/55	0.255	300	99.99580
4	1.1	1947	2.1	12.25	0	75/75	0.255	190	99.97630
8	0.9**	1957	3.1	9.75	0	103/103	0.214	12	99.99984
9	0.8**	1970	2.3	10.50	0	121/121	0.195	8	99.99990
12	1.0**	1860	4.2	11.50	0	90/90	0.234	19	99.99973
14	0.9**	1911	2.0	13.25	0	125/125	0.223	50	99.99936

* Hexane only, 5 X 10⁻⁹ g spike.

** Combustion air preheated to 400°F.

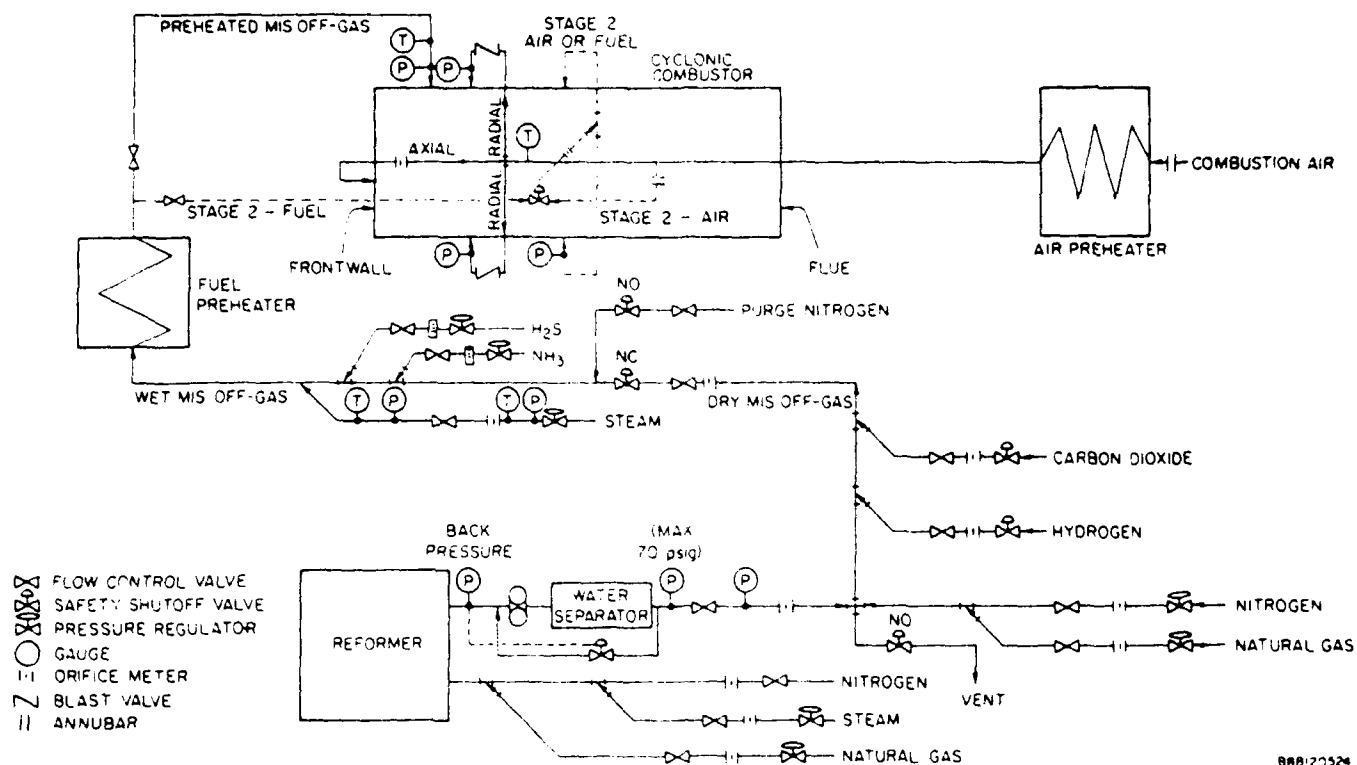
Table 15. RESULTS FOR HEXANE MIXED WITH 1% CCl₄
(by Weight)

Test No.	Firing Rate, 10 ⁶ Btu/h	Thermocouple Base Temp., °F	Exhaust Gas Analysis				CCl ₄ Flow Rate, lb/h	CCl ₄ Recovered, 10 ⁻⁹ µg/20 L	Destruction Efficiency, %
			O ₂ , %	CO ₂ , %	CO, ppm	NO/NO _x , ppm			
1*	0.9**	2001	0.4	11.50	0	84	--	28	--
3	0.9**	1916	2.8	12.25	0	92	0.450	7	99.99995
6†	0.9**	2029	1.9	13.25	0	97	0.413	19	99.99988
9	1.0	2003	2.9	12.25	0	64	0.493	8.4	99.99994
10	1.1	2034	2.0	13.00	0	72	0.536	11	99.99993
12†	1.1	2055	2.2	13.00	0	71	0.550	24	99.99985

* Natural gas fire, no CCl₄, 9 x 10⁻⁹ g spike.

** Combustion air preheated to 400°F.

† Downstream sample.



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Figure 3. FLOW DIAGRAM FOR LOW-BTU GAS TESTS

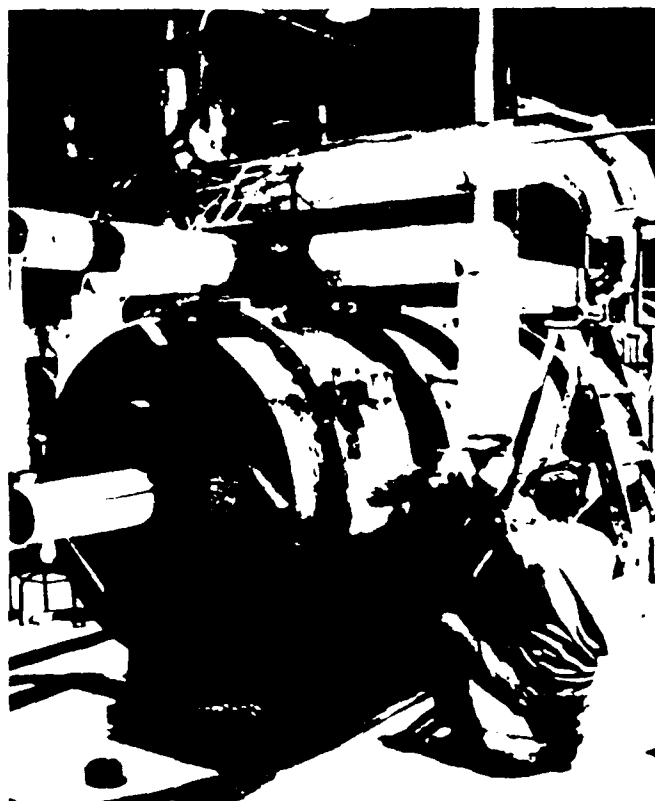


Figure 4. CYCLONIC LOW-BTU GAS COMBUSTOR

Table 16. COMPOSITIONS OF LOW-Btu GASES TESTED

	H ₂	N ₂	CO	CH ₄	CO ₂	H ₂ O, % Wet	HHV, Btu/SCF
	-----		% Dry	-----			
Average	9.2	61.3	1.7	3.7	24.1	7.3	67
Minimum	7.0	59.8	0.5	3.4	29.3	8.7	54

The off-gases for the combustion tests were made first by reforming natural gas and steam in a reformer over a catalyst at 1800°F to generate hydrogen and carbon monoxide. The product gas containing H₂, CO, CO₂, unused H₂O, and small quantities of unused natural gas was quenched in water-cooled heat exchangers. The resulting saturated mixture at about 100°F was compressed to 70 psig, and the condensed water was removed in a water separator. Nitrogen, natural gas, carbon dioxide, hydrogen, steam, ammonia, hydrogen sulfide, and carbon disulfide were blended with the product gas to achieve the required low-Btu gas composition. The higher hydrocarbons were replaced by natural gas.

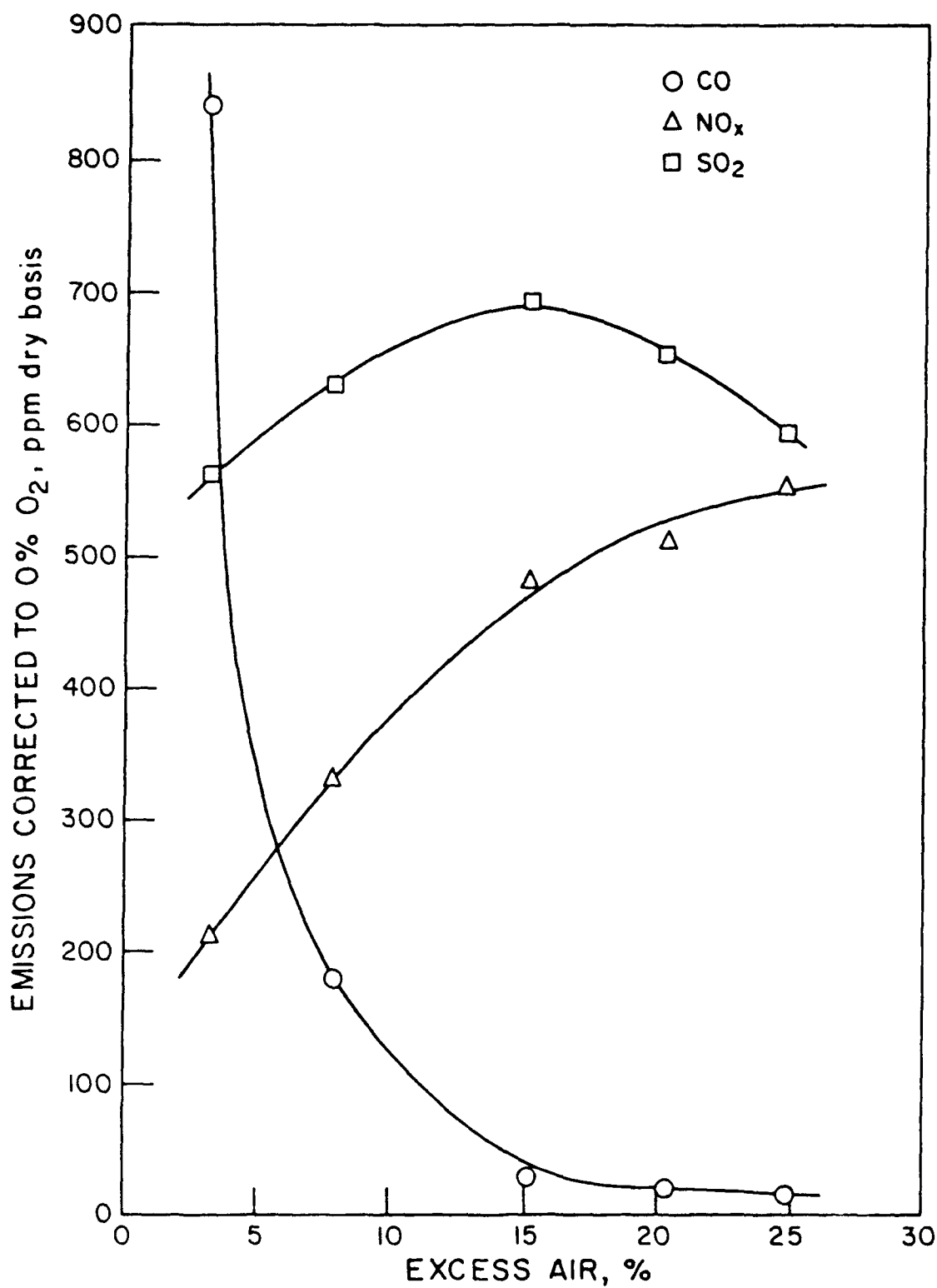
Combustion air and waste were individually preheated in independent natural gas-fired preheaters.

Test Results

At the design firing rate of 3×10^6 Btu/h, the flame with the average heating value gas was unstable until the gas and combustion air were preheated to 335° and 750°F, respectively. At these conditions the combustor wall temperatures stabilized; therefore, a gas temperature of 350°F, an air temperature of 750°F, and a firing rate of 3×10^6 Btu/h were selected as the nominal firing conditions for the combustor performance tests.

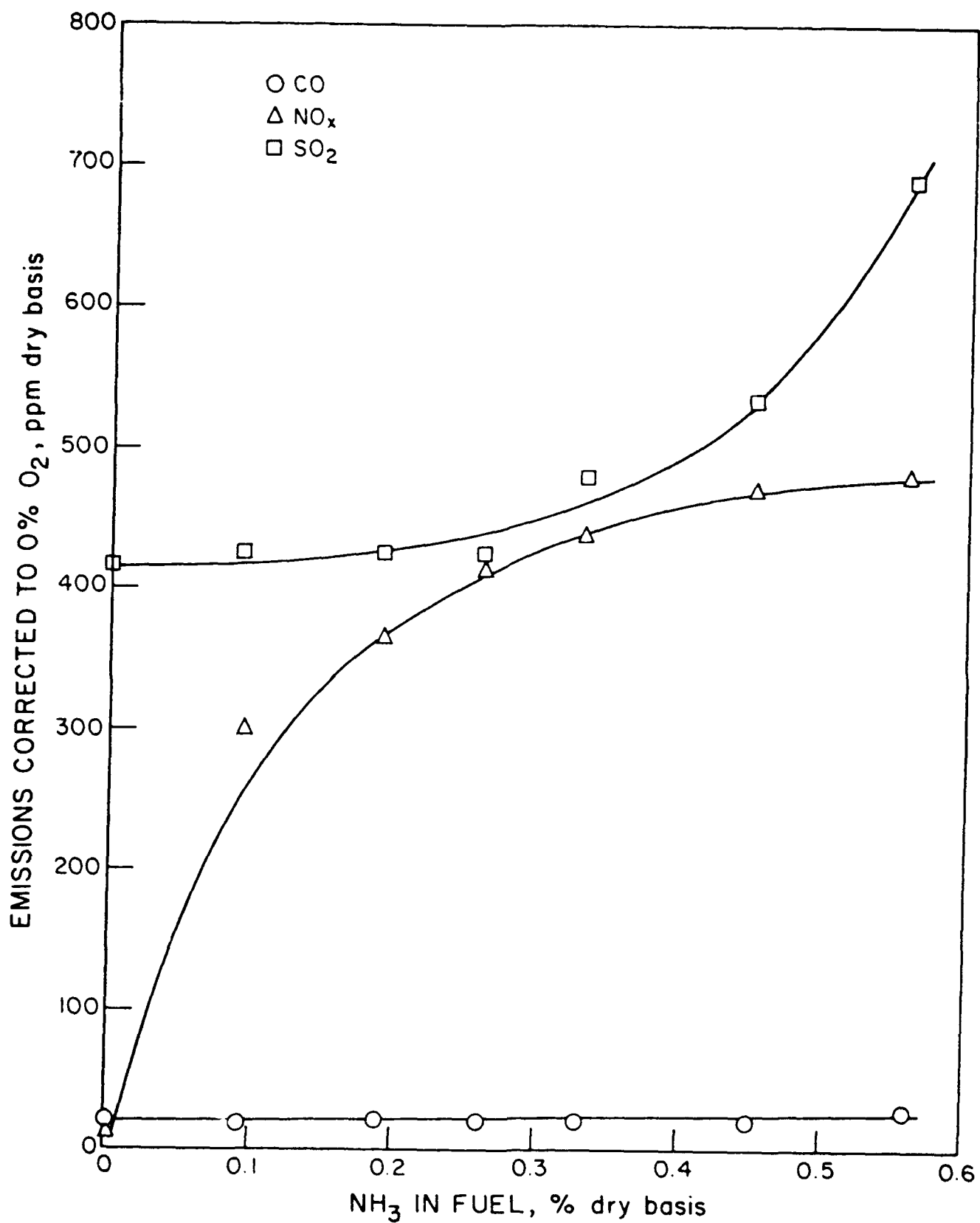
Figure 5 shows the effect of excess air on CO and NO_x emissions in the flue corrected to 0% oxygen. The CO concentration decreased rapidly with an increase of excess air (up to 15% excess air) and then slowly leveled off, whereas the NO_x concentration increased with excess air throughout the range tested. These results are similar to those generally observed with conventional burners.

Figure 6 shows the effect of fuel ammonia concentration on CO and NO_x emissions. The loss in the heating value of the gas at reduced NH₃ concentrations was made up by adding an equal amount (heating value) of natural gas through a calibrated rotameter. The results show that NO_x decreased slowly with a decreasing NH₃ concentration at high waste NH₃ levels and rapidly at low waste NH₃ levels. For example, an 80% reduction in the fuel NH₃ concentration (from 0.5% to 0.1%) reduced NO_x by 40%.



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Figure 5. EFFECT OF EXCESS AIR ON GASEOUS EMISSIONS FOR AVERAGE GAS



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Figure 6. EFFECT OF FUEL NH₃ CONCENTRATION ON EMISSIONS FOR AVERAGE GAS WITH 15% EXCESS AIR

Following the combustor performance tests with the average heating value gas, stability tests were conducted to determine if the cyclonic combustor was capable of burning the minimum heating value gas. The waste gas temperature was increased to 490°F, and the firing rate was reduced to 1.9×10^6 Btu/h. The flame was stable up to 11.3% moisture in the waste, which represents a heating value of 50 Btu/SCF. The waste gas temperature was then slowly reduced. The flame lifted off at a waste gas temperature of 350°F.

The NO_x reduction techniques of combustion air staging and fuel staging were also evaluated separately but were found to be relatively ineffective at the conditions tested.

The major results of the tests with low-Btu off-gas can be summarized as follows:

- The combustor tested is capable of operating on the 67 Btu/SCF off-gas with a stable flame and with low CO (<50 ppm) at the exit at 15% excess air when the combustion air is heated to approximately 750°F and the off-gas is heated to approximately 350°F.
- For NO_x emissions to be below 0.7 lb NO₂ per 10⁶ Btu fuel input, either the combustor should be operated below 7% excess air, which resulted in more than 200 ppm CO, or the off-gas NH₃ concentration should be reduced below 0.1% (dry basis).
- A stable flame can be obtained with an off-design gas (higher moisture content) or a lower heating value gas if the combustor is downrated.
- Fuel staging was not effective in reducing NO_x in that it increased the CO emissions.
- Combustion air staging, as tested, was ineffective in significantly reducing NO_x emissions; however, this technique may be effective if the combustor design is modified for higher first stage temperature and/or larger residence time.
- The test results suggest that the cyclonic combustor performance can be significantly improved by providing better air/waste mixing and by making aerodynamic refinements to the combustor.
- The test results also suggest that the cyclonic combustion approach is well suited for developing an advanced, highly efficient afterburner design for fluidized-bed, rotary kiln, and moving-grate waste combustors, including starved-air designs.

DESIGN AND OPERATION OF THE DEMONSTRATION SYSTEM FOR INDUSTRIAL WASTEWATER NO. 1

Demonstration Cyclonic Waste Combustion System

The development of the cyclonic waste combustor demonstration system was based on the successful results on the pilot-scale unit that were described earlier. On the basis of these data, the demonstration system was jointly designed, constructed, tested, and operated by IGT, York-Shipley, Inc. (Y-S), and an industrial client.



The demonstration system features a compact combustion chamber (Figure 7) with an ash/slag receiver, capable of operating either in dry or slagging mode. The demonstration system has a wastewater handling subsystem and is equipped with a heat recovery boiler, an air heater, and a baghouse. A flow diagram of the demonstration system is shown in Figure 8. Wastewater feeding is automatically controlled by a micromotion flowmeter in the jacketed wastewater conveying jacketed line, traced with 180° to 190°F hot water.

The heat available in the combustor exhaust gases is partially recovered in a two-pass Scotch Marine boiler. Soot blowers, installed for final system operation at the entrance to the convective pass of the boiler, are of concurrent flow, operated on compressed air. In addition, a 12-foot-long, retractable rotary soot blower has been installed to provide for cleaning of the Morison tube and return box of the boiler.

Further heat recovery is provided by an air heater of the basic shell-and-tube heat exchanger design. Preheated combustion air is then conveyed to the combustor and separated into a primary and secondary air stream. The primary air stream is mixed with natural gas, and the gas-air mixture is then injected into the combustor through the top-row tangential nozzles. Secondary combustion air is injected into the combustor through the second row of tangential nozzles. Flow control is accomplished either manually or automatically using an O₂ analyzer installed in the boiler exhaust duct.

Flue gases from the air preheater are cleaned in a baghouse. An induced draft fan mounted on the baghouse support structure pulls exhaust gases through the boiler, air heater, and baghouse. The outlet damper of the ID fan is adjusted manually or controlled automatically to maintain the desired pressure at the inlet of the boiler. Flue gases are then exhausted through the stack to the atmosphere.

System Operation and Test Results

A total of about 175,000 pounds of wastewater was treated during the final 500-hour continuous system operation. Some of the data collected are shown in Table 17. The wastewater averaged a 48.25% solids concentration; its average flow rate was 6.5 lb/min. Therefore, the average waste firing rate was 1.21×10^6 Btu/h. The average natural gas flow was 988 ft³/h for a gas firing rate of 1.04×10^6 Btu/h. The average wastewater/natural gas ratio calculated was 54:46 (Btu basis). It should be noted that a somewhat lower concentration of solids in the wastewater resulted in a significantly higher natural gas consumption. Raising the concentration from 44.2% to 49.2% resulted in about a 26% lower gas consumption.

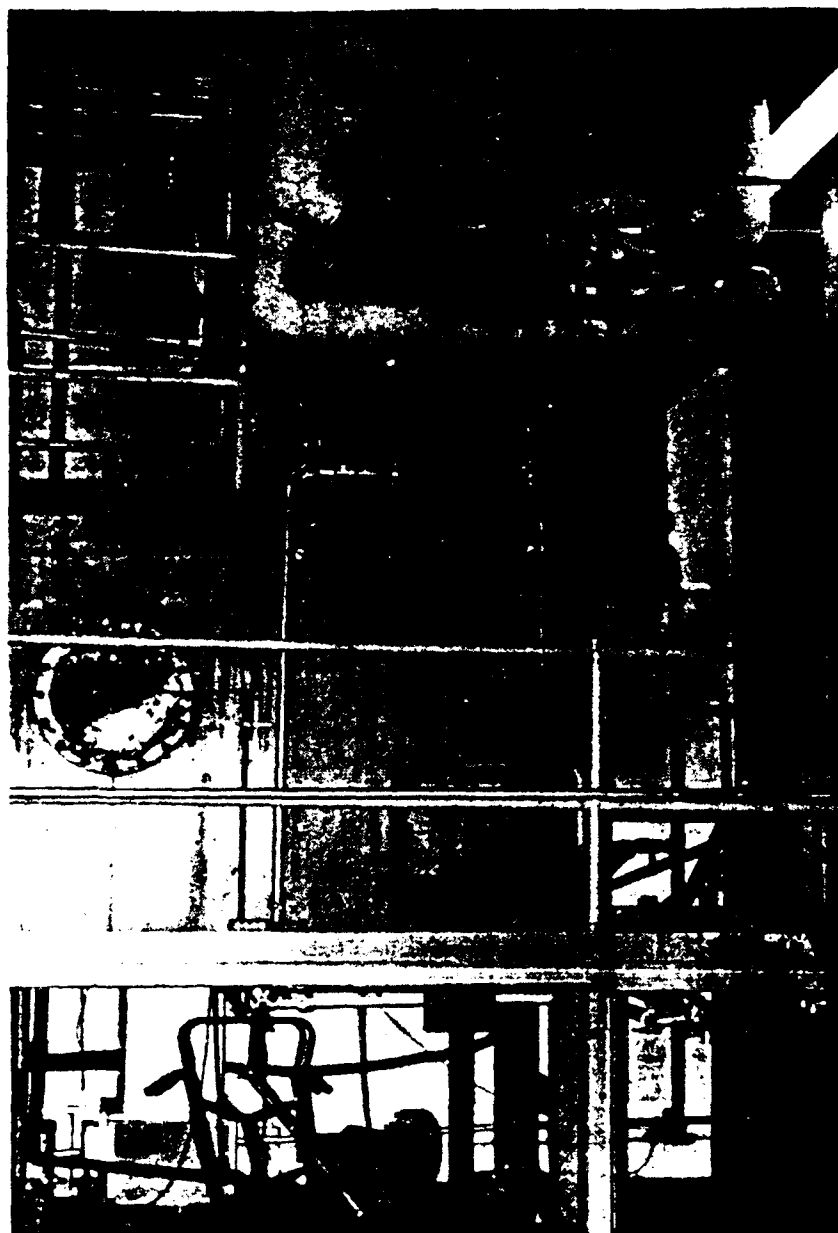
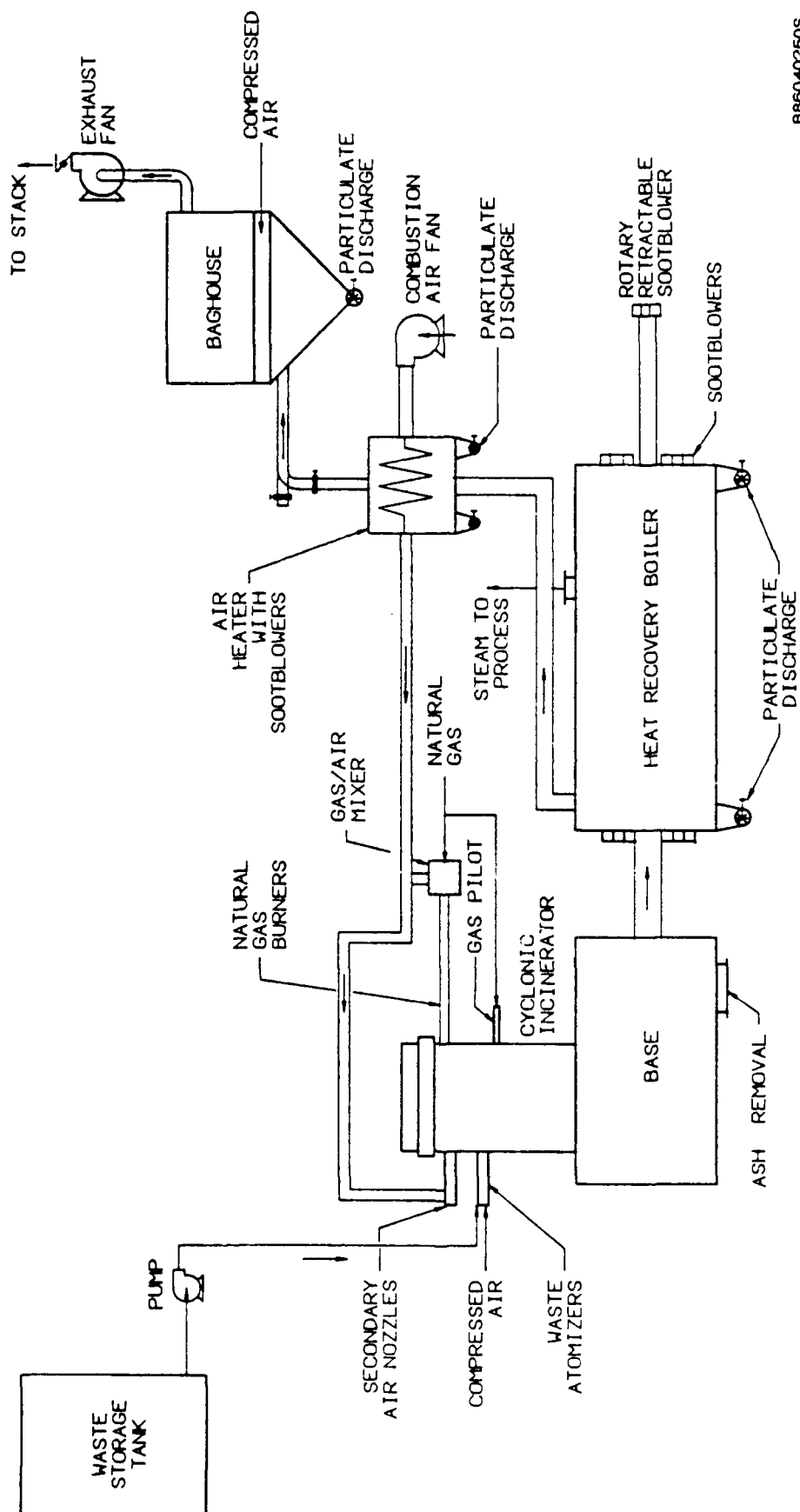


Figure 7. CYCLONIC WASTE COMBUSTION DEMONSTRATION SYSTEM



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Figure 8. CYCLONIC WASTE COMBUSTION DEMONSTRATION SYSTEM FLOW DIAGRAM

Table 17. DATA COLLECTED DURING THE 500-HOUR CONTINUOUS SYSTEM OPERATION

Test No.	Natural Gas Firing Rate, SCF/h	Liquid Waste Flow, lb/min	Temperature, °F				Flue Gas Analysis	
			Incinerator Base	Boiler Morison Tube Exit Thermocouple	Boiler Exit	Baghouse Inlet	Combustion Air	Combustion Air/Natural Gas Mixture
1	1300	6.7	1970	1110	553	320	329	294
3	1195	6.7	2020	1065	526	335	284	252
5	840	7.0	2080	1090	561	350	287	257
7	836	6.5	2200	1075	546	330	274	238
10	851	6.6	2150	1644	532	320	281	241
12	851	6.5	2000	1006	488	310	278	216
16	933	6.5	2130	955	519	320	284	248
18	963	6.5	2100	1150	537	320	298	262
20	1088	6.5	2175	5954	511	330	297	259
21	1163	5.0	2150	950	493	310	278	239
22	961	6.0	2190	950	498	310	277	229
23	922	6.0	1950	950	477	315	284	225

Flue Gas Analysis
O₂, %
CO, ppm

To avoid incomplete combustion, the combustor base temperature (Figure 9) was maintained at a higher level than in the past. The temperature of the flue gases exiting the Morison tube was monitored continuously.

The major results of the system operation can be summarized as follows:

- The demonstration system proved to be a reliable and highly efficient operation, with low-emission combustion of wastewater with an HHV of about 3000 Btu/lb.
- The heat contribution ratio of wastewater to auxiliary fuel averaged 55:45.
- Major operating parameters during the final operation included 2.15×10^6 Btu/h total firing rate, 2050°F combustion temperature, air preheat of 325°F, and specific heat release of 0.12×10^6 Btu/h with 20% excess air. Carbon monoxide concentration in the flue gas was usually below 100 ppm.
- It was demonstrated that the flue gas temperature control after the radiative chamber (appropriate surface area and surface cleaning) is a key element in eliminating the fouling and slagging of the first convective pass.
- For the last 24 hours of the final operation, mechanical wastewater atomizers operating at 100 psig were used. There was no apparent problem with the mechanical atomization during this period. Mechanical atomization has a good potential for commercial cyclonic waste combustion systems.

Data collected provide a sufficient data base for a larger size commercial system design (from 10×10^6 to 25×10^6 Btu/h total firing rate).

IGT CYCLONIC WASTE COMBUSTION MODULAR TEST FACILITY

The successful results described above have led to the design and construction of a modular cyclonic waste combustion test facility at IGT's Energy Development Center. As illustrated schematically in Figure 10, it consists of the following subsystems:

- Advanced, highly flexible, cyclonic waste combustor
- Liquid waste feeding system
- Gaseous waste feeding system
- Solid waste feeding system
- Main auxiliary fuel system (natural gas)
- Combustion air system (air temperature from ambient to 1200°F)
- Oxygen enrichment system

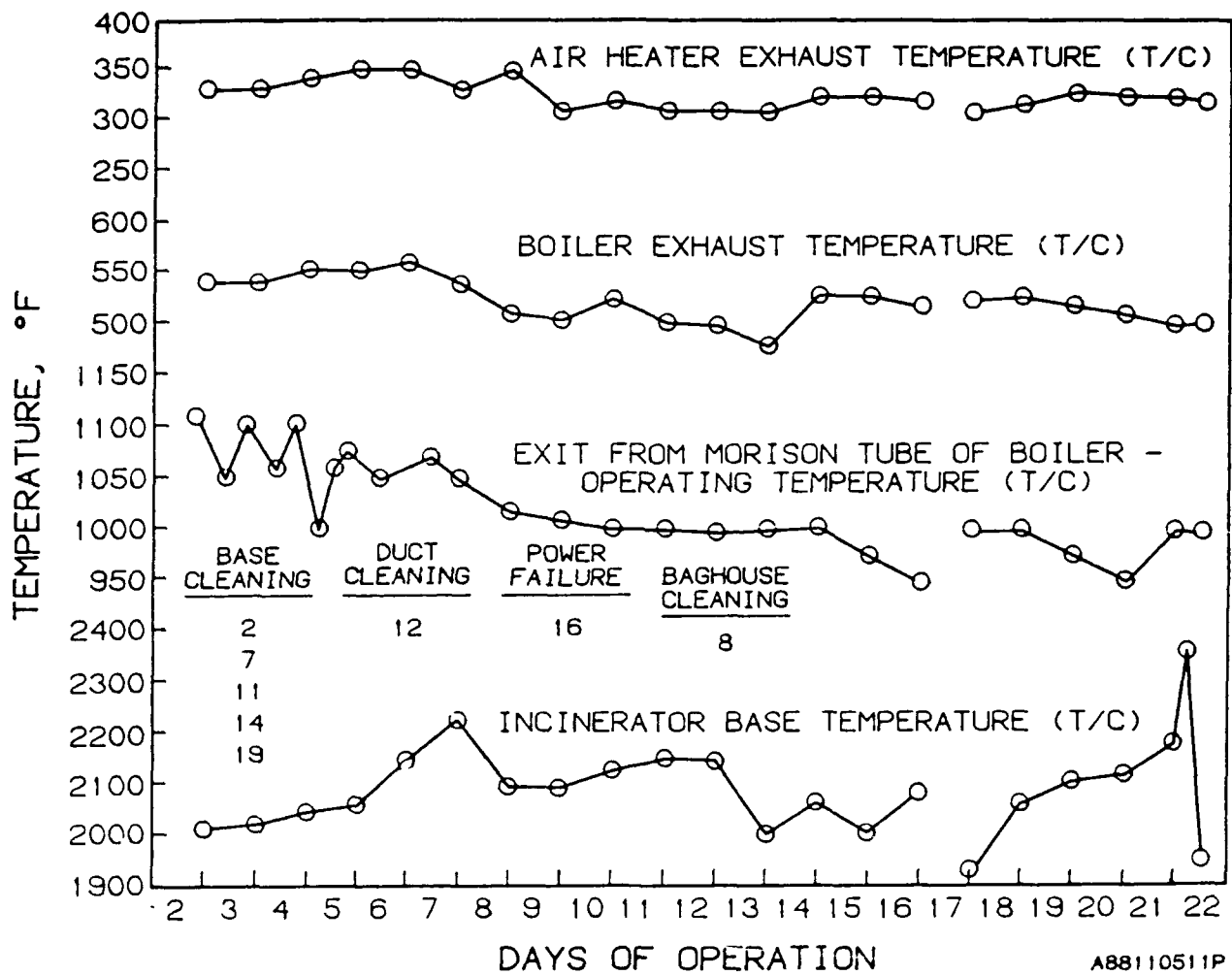


Figure 9. COMBUSTOR BASE, BOILER, AND AIR HEATER FLUE GAS TEMPERATURES AS A FUNCTION OF OPERATING TIME (500-hour Operation)



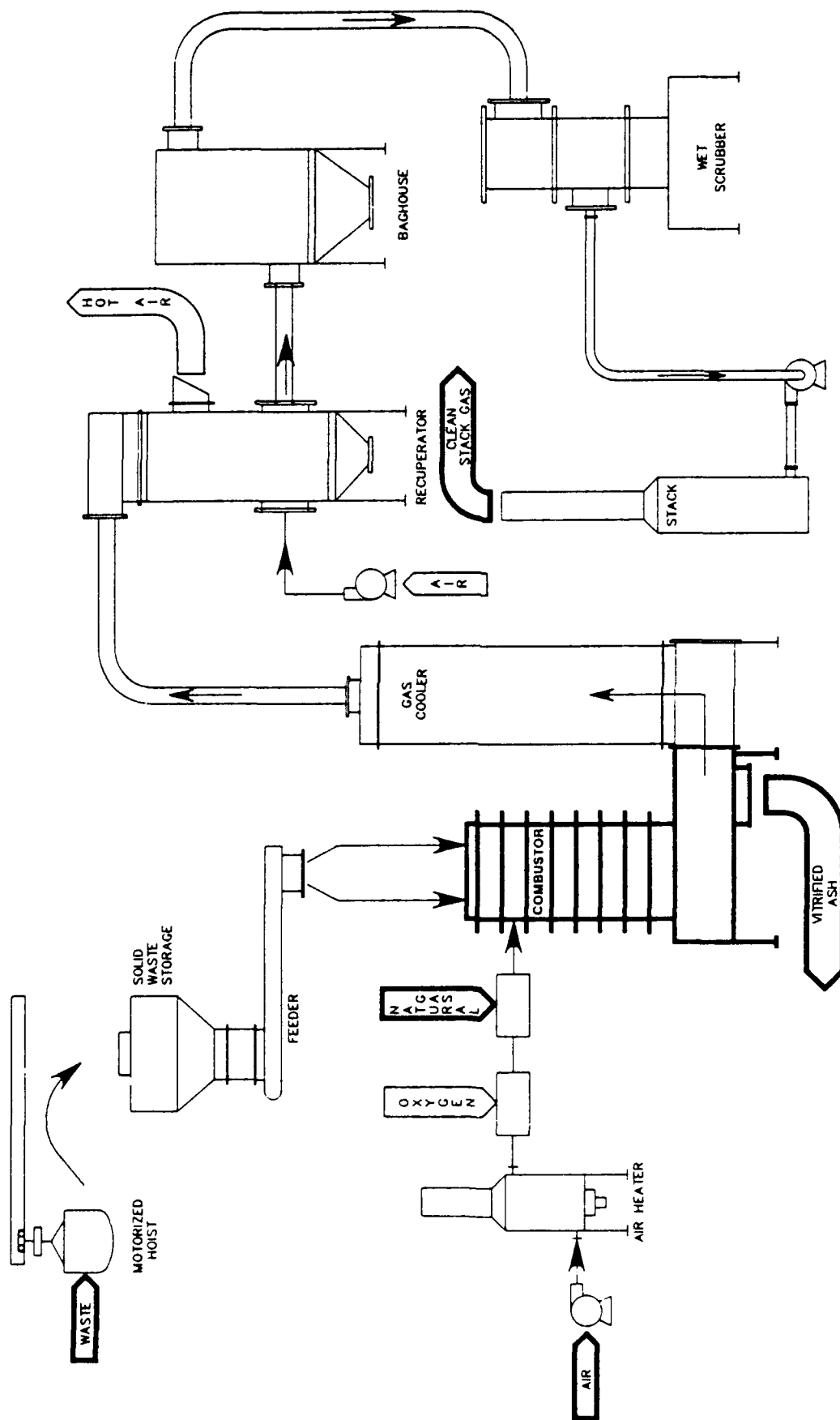


Figure 10. SIMPLIFIED FLOW DIAGRAM OF THE CYCLONIC WASTE COMBUSTOR TEST FACILITY

- Exhaust gas treatment system
 - Direct quencher
 - Recuperator
 - Baghouse
 - Scrubber
- Ash (slag) removal system
- Control systems
 - Semiautomatic control
 - Probes and instrumentation
 - Computer data acquisition.

The heart of the test facility is the cyclonic waste combustor (Figures 10 and 11). For versatility, similar to the earlier pilot unit, the design incorporates the use of interchangeable cylindrical sections to evaluate combustion performance, depending on the characteristics of the specific waste being combusted. Some of the sections are refractory-lined, and other sections incorporate a water-cooled annulus and an interior refractory lining.

The waste feeding systems associated with the cyclonic combustion unit consist of a solid waste feeding system and a liquid waste feeding system. The solid waste feeding system (Figure 12) is an automatic waste delivery system that meters the amount of solid waste being combusted. The waste is delivered to the combustor through ports located in the lid of the combustor. The liquid waste feeding system is also an automated system. The feed storage includes mixing, recycle, and heating capabilities to assure uniformity of the waste being incinerated. The waste is then delivered for injection into the combustor via liquid waste atomizers. Compressed air or steam for pneumatic atomization, or a high-pressure pump for mechanical atomization, are also available. Tangential or radial injection ports of the combustor are selected, depending on the quality (amount of water, heating value, etc.) of the waste being treated.

An auxiliary fuel system provides a natural gas supply that can be either premixed with air or injected through the appropriate nozzles. If required, oil can be used as an auxiliary fuel.

The combustion air system provides ambient or preheated primary and secondary air with a preheat temperature up to 1200°F. The oxygen enrichment system provides delivery and injection of pure oxygen to the primary and secondary air supply lines.

Downstream of the cyclonic combustion unit is exhaust gas treatment equipment (Figures 10 and 11) consisting of a direct quencher, convective air heater, baghouse, and scrubber. Provisions were made to add a heat recovery boiler and a high-temperature radiative recuperator to the exhaust gas treatment system at a later date.



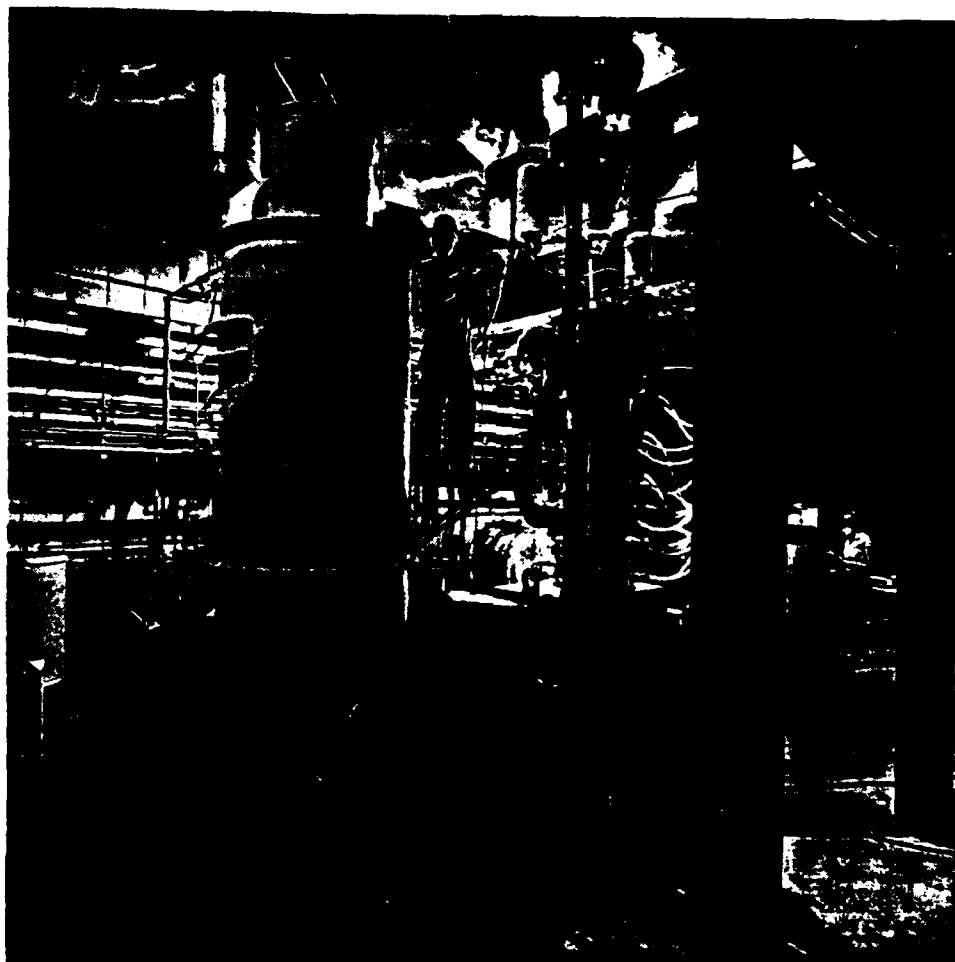


Figure 11. CYCLONIC WASTE COMBUSTOR AND
EXHAUST GAS DIRECT QUENCHER



Figure 12. SOLID WASTE FEEDING SYSTEM, SCRUBBER,
BAGHOUSE, AND AIR HEATER

A semiautomatic, computer-assisted control system ties the individual components and subsystems of the test facility connects and provides computerized data acquisition. It is centrally located in the control room, where the desired operation and safety aspects of every component of the facility are being initiated and monitored.

The facility is equipped with a full range of analytical instrumentation for continuous monitoring of the flue gas emissions: O_2 , CO, total hydrocarbons (THC), NO_x , SO_x , etc.

THERMAL TREATMENT OF SPENT ALUMINUM POTLINERS

The efforts thus far had been directed toward the development of a general cyclonic waste combustion system for industrial applications. The focus had been on dry ash discharge; however, as discussed earlier, exploratory tests with molten ash discharge also showed good potential. To further evaluate this mode of operation, a project was initiated with funding support from the gas industry.*

The objective was to evaluate the waste combustor using a solid feed-type waste, with both organic content and inorganic content, to demonstrate its destruction capability and the slagging performance.

Solid feed-type wastes are anticipated to be a major portion of the candidate wastes for application of this technology. Specifically, spent potliners (SPL), a major waste product of the aluminum smelting industry were selected for the proof-of-concept testing. Potliners, comprising carbon and refractory material, are used as an electrolytic cathode and insulating material in large reinforced steel cells or pots that contain cryolite (Na_3AlF_6), alumina (Al_2O_3), and various additives. In these pots, calcined alumina is electrolytically reduced to molten aluminum metal and subsequently drawn off. During this process, carbon in the potliner combines at high temperatures with nitrogen to form cyanide that is absorbed in the liner itself.

After a few years, the potliners crack and must be replaced. In addition to cyanides, the SPL contain a significant amount of leachable fluorides. Table 18 shows the composition of SPL from two aluminum producers that annually amounts to roughly 150,000 tons of waste material, which must be either discarded, destroyed, or reclaimed in a manner that prevents the cyanides, fluorides, and other organic and inorganic impurities from reaching the environment. For many years, SPL were recycled to recover cryolite, using one or more of several different recovery schemes. Landfill disposal is not acceptable environmentally.

* GRI, Enron Corp., Northwest Pipeline Corp., Tenneco, and IGT Sustaining Membership Program.

Table 18 . REPORTED COMPOSITIONS OF SPL

<u>Constituent</u>	<u>Alcoa</u>	<u>Reynolds</u>
C	28.6	42.7
Al	14.2	4.7
Si	4.76	0.11
Fe	3.23	0.27
Na	13.9	20.0
F	18.2	17.6
CN	0.09	0.135
Al Carbide	0.46	--

In recent years, indoor storage has provided a temporary means of accumulating SPL at some smelter locations until an acceptable or final disposal option becomes available. Thermal treatment using fluidized-bed techniques has been tried in the past, but with little success; thermal decomposition of cyanide is successful, but leachable fluoride content has not been reduced to environmentally acceptable levels. Recently it has become a federally listed hazardous waste.

The slagging mode treatment of SPL is shown conceptually in Figure 13. In this mode, the waste is burned and the inorganic content (ash) is melted primarily in the space. The resultant particulates and droplets are separated from the combustion products and thrown on the combustion chamber walls by the centrifugal forces created by the cyclonic motion. Final burnout and melting occurs on the refractory walls, producing a thin layer of slag that flows down into the slag received and is removed by gravity.

In this mode, the cyclonic combustor is believed to be capable of treating a wide variety of solid, liquid, and gaseous wastes and offers great operational flexibility. The thermal and combustion characteristics are controllable and can be tailored to specific wastes. The controlling parameters are the injector configurations, the amounts of the primary air, secondary air, natural gas, and waste, and the orifice size and location. The sectional design of the pilot-scale combustor with multiple injection ports simplifies the adjustments of these parameters.

The specific performance goals of the test program are to achieve a DRE of 99.999% of cyanides and 90% ash removal as slag, while operating with less than 20% excess air and producing air emissions of less than 25 ppm carbon monoxide and less than 25 ppm total hydrocarbons.

Current Status

The system has been configured for the treatment of SPL with molten ash discharge, and a system shakedown (without waste feed) has been carried out firing natural gas. Two



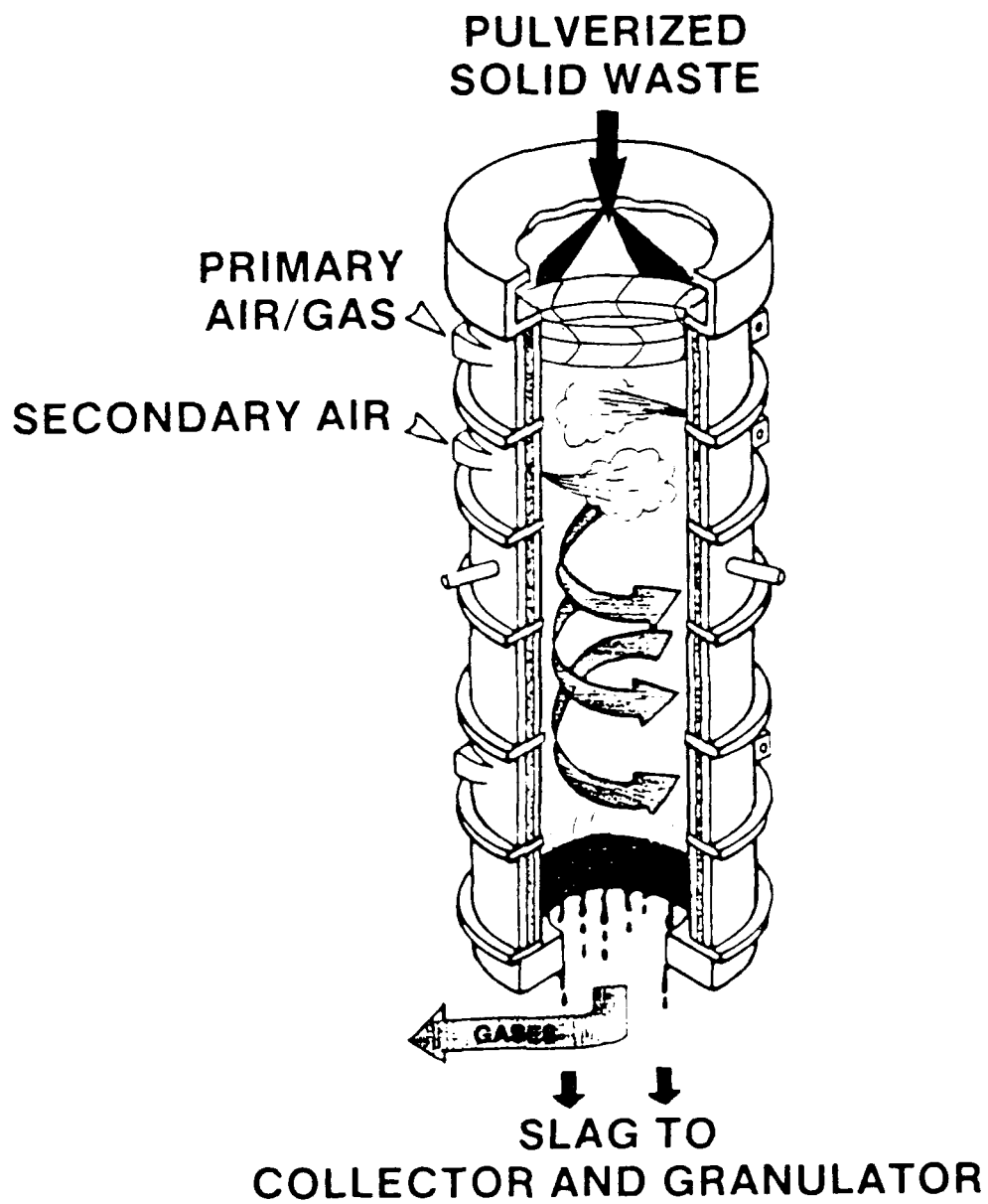


Figure 13. SLAGGING CYCLONIC WASTE COMBUSTION

relatively inexpensive fluxes have also been identified, through analytical studies, that could significantly reduce the SPL ash melting temperatures. Testing is expected to be completed during 1991. If successful, a full-scale field evaluations would be undertaken during 1992/93.



EFFECT OF ORGANIC RESIDUES ON TOLERANCE OF PLANTS TO TNT TREATED SOILS AND ON THE RECOVERY OF TNT FROM SOILS

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ABSTRACT

Explosives contaminated soils can result in barren areas that are subject to wind and water erosion and offsite movement of contaminants. A greenhouse study was carried out to examine the growth of potential cover crops planted on TNT treated soils. Initial levels of TNT in the soil were 1000 and 2000 mg/kg on a dry weight basis. These levels were achieved either by spiking uncontaminated soils with munitions grade TNT or by mixing highly contaminated soil (approximately 22,000 mg/kg TNT) from a contaminated field site with uncontaminated soil. Soils were amended with 0, 5, 10 and 20% (by weight) dried and ground residues of wheat straw alone and in combination with alfalfa. Visual ratings, plant height, and dry matter production of the test species were dramatically improved with the addition of organic residues to soil. Little or no growth occurred in the unamended soils while the addition of 5% ground wheat straw resulted in considerable growth and the addition of 10% or more amendment to TNT treated soils resulted in dry matter accumulation for all test species that was in most cases not significantly different from the control. Of the species tested perennial ryegrass was the species most tolerant to TNT treated soils and resulted in the greatest dry matter production while alfalfa appeared to be the least tolerant species. Soil extractable levels of TNT decreased rapidly with time in all soils. The addition of organic residues enhanced the rate of disappearance of extractable TNT compared to unamended soils. After 90 days of growth the extractable levels of TNT in soils originally containing 2000 mg/kg TNT which were also amended with alfalfa or wheat straw was less than 2% of the initial value. By contrast recovery of TNT from soils not amended with ground wheat straw or alfalfa was approximately 15-60%. The concentration of extractable TNT at the end of the experiment for soils prepared by mixing highly contaminated soil from the field were higher than for soils prepared by the addition of munitions grade TNT but plant growth was not significantly different.

EFFECT OF ORGANIC RESIDUES ON TOLERANCE OF PLANTS TO TNT TREATED SOILS AND ON THE RECOVERY OF TNT FROM SOILS

Introduction

The U.S. Army had numerous explosive production facilities nationwide, all in full scale production more than four decades ago, during World War II. Contamination of land, water and air by the residues of explosives such as TNT has inadvertently occurred in a variety of situations. Disposal or reduction of levels of explosives residues in an environmentally acceptable manner is currently a key challenge. Lack of a comprehensive explosives waste disposal program in the past resulted in the accumulation of residues in holding ponds, ditches prepared for land application, and other places. The result is extensive quantities of material in high concentrations distributed over small land areas in some locations and lower but significant concentrations of explosives over larger areas of land.

Perhaps the most immediate concern are those areas where the concentrations of residual explosives are large enough to prevent vegetative cover. The barren soils represent a very real potential for offsite movement of explosives residues via wind and water erosion. Because the chemical properties of many explosives result in fairly strong binding to soils, particularly the organic matter portion of soils, it is the movement of soil particles and associated explosives that presents a hazard to offsite soil and surface water contamination.

Studies on the health-hazard and environmental toxicity of TNT and metabolites have been undertaken by several Army laboratories (Won et al. 1976; Wentzel et al. 1975; McCormick et al. 1978; Burrows and Dacre, 1975; Kaplan and Kaplan 1982 a-d). Previous research has shown TNT to be toxic to higher plants (Palazzo and Leggett 1983, 1986 and Schott and Worthley 1974), algae (Liu et al 1976, Smoch et al 1976 and Won et al 1976), bacteria (Klausmeier et al 1973), and microorganisms (Enzinger 1971 and Nay et al 1974). A number of aquatic surveys of streams have shown that the discharge of ammunition waste results in changes in or losses to downstream biological communities.

Remedial cleanup of contaminated sites has been the objective of research conducted by USATHAMA and others (Pardee and Hodge, 1967; Osmon and Andrews, 1978; Kaplan and Kaplan, 1982 a-d, 1983; Kaplan et al., 1985) on the best available and economically sound treatment technologies. Any remedial action that can provide ground cover for barren soils also greatly reduces the risk of movement of bound organics by water or by wind erosion. Thus the establishment of vegetative cover should be a high priority in the stabilization of lands

Mention of a proprietary product does not constitute an endorsement or a recommendation for its use by the authors.

contaminated with explosives. In addition to the benefits of reduced erosion, metabolism and breakdown of TNT and other nitro compounds has been shown to occur in higher plants (Palazzo and Leggett, 1986; Shimabukuro et al., 1982), lower plants (Parrish, 1977), and bacteria (Jerger et al., 1976; McCormick et al., 1978), suggesting the possibility of bioremediation.

On site remediation is usually a more cost effective method of land stabilization and revegetation than land removal and treatment. On site treatment includes acceleration of processes that reduce the toxicity of TNT or other residues to plants, thus encouraging vegetative growth. Direct processes that may facilitate reduced TNT toxicity to vegetation are increases in soil temperature, moisture, light, air, soil organic matter and/or changes in soil pH. Specific processes which may facilitate explosives breakdown include metabolism by soil biota in conjunction with cultural techniques such as tillage, which can incorporate oxidizable residues or alter soil temperature, moisture, and aeration. Similar processes have been explored for degradation of high concentrations of pesticide contaminants in soils (Felsot and Dzantor, 1991). The studies described in this paper were undertaken to address the question of revegetation and stabilization of TNT contaminated landscapes by examining the effect of organic amendments of the tolerance of plants to soils containing TNT and on the recovery of extractable TNT from these soils.

Materials and Methods

This greenhouse study examined the response of three plant species to 2,4,6-trinitrotoluene (TNT) contaminated and amended soils. Plants were grown for 90 days in greenhouses in plastic pots. Initial soil levels for TNT of 1000 and 2000 mg/kg of TNT were obtained either by dissolving crystalline TNT in acetonitrile (ACN) and applying by spray application to the soil (hereafter referred to as spiked soil) or by mixing highly contaminated field soil from a former munitions production and recycling area with uncontaminated soil to obtain the desired initial TNT level (hereafter referred to as cut soil). At each rate of TNT, there were six different amounts of amendment added. The amendments were wheat straw and alfalfa at the following combinations as a percentage of total dry weight: 0% wheat and 0% alfalfa, 5% wheat and 0% alfalfa, 5% wheat and 5% alfalfa, 10% wheat and 0% alfalfa, 10% wheat and 10% alfalfa, and 20% wheat and 0% alfalfa. A pot containing 1000 mg/kg TNT, 10% wheat straw and 10% oat straw, for example, consisted of approximately 300 grams of soil, 37.5 grams each of air-dry wheat straw and ground alfalfa, and 0.375 grams of pure TNT equivalent. There were three replications of each treatment and the treatments were arranged in a randomized complete block design.

The contaminated soil used in this study was originally an Elliot silt loam (fine, illitic, mesic Aquic Arigidoll), collected from Group 61 at the Joliet Army Ammunition Plant. Group



61 was an area shaped into ridges and furrows with the furrows being used for waste water disposal during recycling of munitions. The surface soil from the contaminated area, however, appeared to have been reworked during development and may have also been subject to considerable erosion. The concentration of TNT in this soil as collected was approximately 20,000 mg/kg as measured by ACN extraction and HPLC analysis. It was collected from the furrows of the Group 61 area to a depth of approximately 10-15 cm, allowed to air-dry and stored in Rubbermaid™ (Rubbermaid, Wooster, OH) containers until used in this study.

Uncontaminated soil from the surface 15 cm of an Elliot silt loam from a field near Group 61 was collected as a control, allowed to air-dry, and stored in Rubbermaid™ containers until used. All soils were ground by hand and/or in a soil grinder (Dynacrush 2, Dayton Electric Mfg. Co., Chicago IL) to pass through a 4 mm sieve.

Before any amendments were incorporated, the soils designated as spiked were treated with appropriate amounts of crystalline TNT that had been dissolved in ACN to result in a final soil level of TNT that would be 1000 or 2000 mg/kg on a total dry weight basis. Appropriate amounts of 2,4,6-TNT were dissolved in approximately 100 ml of acetonitrile and applied to 10 kg of bulk air-dry soil using an aspirator. The soil was mixed in a rotating stainless steel drum during and after the ACN containing TNT was applied. All treated soils were allowed to sit at least overnight to allow the solvent used to evaporate. The cut soil was prepared by mixing appropriate amounts of highly contaminated soil with uncontaminated soil to achieve initial TNT soil levels of approximately 1000 and 2000 mg/kg.

The crystalline TNT for spiking was obtained from the Joliet Army Ammunition Plant, Joliet, IL. High performance liquid chromatography (HPLC) analysis determined this lot of munitions-grade TNT to be 92.5% pure as compared to the TNT standard analytical reference material (SARM) from the Picatinny Arsenal. The amount of TNT added to spiked soils was adjusted for compound purity.

Plant species used in this study included sorghum/sudangrass (*Sorghum x sudanense* cv 73-804 FS), alfalfa (*Medicago sativa* cv WL320), and perennial ryegrass (*Lolium perenne* cv Manhattan II). These species were selected from among more than thirty species or cultivars tested for tolerance to TNT in a previous study.

After spiked or cut soils were prepared appropriate amounts of amendments were added to achieve the percentage amendment level desired. Amendments were thoroughly mixed with soil and added to 11.25 cm round black plastic pots (Belden Plastics, St. Paul, MN). Each pot received 150 to 300 ml of water, depending on the amount of amendment added, 24 hours before planting. A preweighed amount of seed was scattered in each pot and a thin layer of appropriately amended soil used to cover the seed. The amount of seed sown (g/pot) was 1.75g of sorghum, 0.60g of alfalfa, and 1.75g of perennial ryegrass. Each pot was watered with a pressurized sprayer to keep the surface of the pots moist and to prevent soil crusting until plants

had emerged. After emergence, pots were watered with distilled water containing diluted (4g/l) of Peters 20-20-20 fertilizer solution (Peters, Fogelsville, PA). As the plants grew the concentration of fertilizer was doubled.

Samples from each of the amended soil preparations were analyzed for initial TNT content before wetting or planting. Unseeded pots containing soil from each of the thirty treatments were placed in the greenhouse to study the recovery of TNT with time. These pots were watered and treated similar to planted pots, except that soil samples were taken periodically for TNT analysis. For this analysis, two grams of air-dry soil and 20 ml of acetonitrile were placed in a 25ml glass screw-cap culture tube. The soil was dispersed for one minute using a vortex mixer, or by hand. Tubes were sonicated for 18 hours or more in a water bath. Following sonication, a 10 ml aliquot of sample was combined with 10 ml of aqueous calcium chloride solution, and left standing for at least 15 minutes. An aliquot of the supernatant was filtered through a 0.2 μm regenerated cellulose filter prior to analysis. Analysis was accomplished by using a Beckman HPLC system fitted with a micromeritics autosampler. Fifty μl of filtered extract was injected onto a 4-5cm C-18 guard column and a 25cm analytical column. The mobile phase was 60/40 (v/v) methanol/water at a flow rate of 1.5 mls/min. Compounds are detected at 254nm and peak heights used to quantify explosive levels. The soils were extracted as soon as possible after sampling and stored in the freezer until analysis for TNT. After the final plant harvest, soil from each pot was extracted for TNT analysis.

Plant heights and visual ratings were recorded periodically over the 90 day study. A visual rating scale was developed, with a range from 0 to 10 (Table 1). Zero represented no evidence of germination and 10 represented excellent growth. After each harvest plants were cut with a scissors approximately 3 cm or higher above the soil and plant fresh weights were determined. Clipped plant material was oven-dried at 65°C for 48 hours and dry weights recorded.

Statistical analyses were performed using MSTAT (Version 4.0, Michigan State University, 1986). Each species was analyzed independently as a randomized complete block design with three replications and thirty treatments.

Results and Discussion

Alfalfa. Results for visual ratings and plant height for alfalfa are given in Table 2. Pots containing spiked or cut soils with no amendments exhibited visual symptoms of severe stress 14 days after planting and were essentially dead 89 days after planting. Where 5% wheat straw only was added, the plants treated with 2000 mg/kg TNT (both spiked and cut) were showing visual stress signs 14 days after planting but failed to show similar stress by the fourth harvest (89 days after planting). As discussed later this lack of stress in the later stages of the experiment was associated with decreased levels of extractable TNT in the soil. Where any



Table 1. Visual rating scale

Rating	Description
10	Excellent Growth
9	Slightly less than excellent growth
8	Plants visibly shorter - look healthy
7	Some stress obvious
6	General Stress obvious
5	Very stunted growth
4	Plants beginning to die
3	Severe stress - plants will die
2	Death/dying after limited growth
1	Death after germination
0	No evidence of germination

combination of 10% or more total amendment or more had been added, the plants appeared quite healthy, particularly by the final harvest. Plant height measurements are consistent with the visual results just discussed (Table 2). The oven-dry yield of Alfalfa 320 for all harvests was significantly different from the zero TNT treatments only when no amendments were added and at the 2000 mg/kg spike TNT treatment with 5% wheat straw amendment (Table 3). Where soils were not amended, alfalfa plants died soon after germination and no harvest was possible. In general, plants grown in pots initially containing 2000 mg/kg TNT resulted in slightly lower dry matter production but these differences were not statistically significant. Addition of ground alfalfa to soil in which alfalfa seedlings are grown presents the possibility of allelopathic autotoxicity but the results from this experiment show no significant or consistent difference between a mixture of wheat straw and alfalfa or wheat straw alone. Both were effective in significantly improving plant growth compared to the unamended soils.

Sorghum/sudangrass. Sorghum/sudangrass was somewhat more tolerant to TNT amended soils than was alfalfa. Even where no amendments were added plants did not die (Table 4) although they exhibited severe stress (visual ratings of 4.5 or less in most cases) through the three month growing period. Consistent with alfalfa, plants grown on soils with initial TNT levels of 2000 mg/kg and 5% wheat straw showed severe stress symptoms and were significantly shorter 14 days after planting than those on soils not treated with TNT. Soils amended with a total of 10% or more amendments frequently resulted in plants with much higher visual ratings and significantly taller than the zero amendment treatment, but not

Table 2. Visual ratings and plant height of alfalfa (*Medicago sativa* cv WL320) at 14 and 89 days after planting (DAP) on TNT contaminated soils with various organic amendments.

Initial Soil ¹ TNT(mg/kg)	Amendment ² (%)	---Visual Ratings---		---Plant Height(cm)---	
		14 DAP	89 DAP	14 DAP	89 DAP
0	0 W 0 A	10.0	10.0	5.8	11.7
0	5 W 0 A	9.0	8.3	4.8	9.7
0	5 W 5 A	10.0	7.7	5.7	8.2
0	10 W 0 A	9.7	9.0	4.7\$	10.3
0	10 W 10 A	10.0	9.0	5.5	10.2
0	20 W 0 A	10.0	10.0	5.0	11.3
1000s	0 W 0 A	2.0	1.3	0.7*	0.8*
1000s	5 W 0 A	6.7	10.0	3.1*\$	12.7\$
1000s	5 W 5 A	10.0	9.0	4.5*\$	10.7\$
1000s	10 W 0 A	8.0	9.5	4.0\$	11.0\$
1000s	10 W 10 A	8.7	10.0	6.0\$	14.2\$
1000s	20 W 0 A	9.5	10.0	5.3\$	12.5\$
2000s	0 W 0 A	2.0	1.7	0.7*	0.0*
2000s	5 W 0 A	3.7	8.3	2.1*\$	8.5\$
2000s	5 W 5 A	7.2	9.3	4.2*\$	9.7\$
2000s	10 W 0 A	7.3	8.3	3.8\$	8.8\$
2000s	10 W 10 A	7.2	9.7	4.8\$	13.7\$
2000s	20 W 0 A	8.3	7.3	4.7\$	8.7\$
1000c	0 W 0 A	3.0	1.3	1.1*	0.7*
1000c	5 W 0 A	9.3	8.7	4.8\$	9.3\$
1000c	5 W 5 A	9.7	9.3	4.8\$	10.3\$
1000c	10 W 0 A	10.0	9.3	4.8\$	9.3\$
1000c	10 W 10 A	8.5	8.3	5.5\$	10.7\$
1000c	20 W 0 A	9.3	8.7	4.3\$	10.0\$
2000c	0 W 0 A	2.5	1.3	1.0*	0.0*
2000c	5 W 0 A	5.7	9.0	3.2*\$	9.5\$
2000c	5 W 5 A	8.3	9.3	4.7\$	11.3\$
2000c	10 W 0 A	6.7	8.7	3.3*\$	10.3\$
2000c	10 W 10 A	9.2	10.0	5.5\$	11.2\$
2000c	20 W 0 A	9.7	10.0	4.2\$	12.0\$

LSD(0.01) 1.07 4.91

\$ = Sig. vs no amend, same TNT level and type ; * = Sig. vs no TNT, same amend level and type.

¹ Numbers followed by s are for soils spiked with TNT and numbers followed by c are for cut soils (highly contaminated field soils mixed with uncontaminated soil to achieve the desired initial TNT level).

² Number indicates % (by dry weight) of wheat straw (W) or alfalfa (A) mixed with the soil.



Table 3. Total Oven-dry weight (g/pot) for all harvests of alfalfa (*Medicago sativa* cv WL320) from TNT contaminated soils with various organic amendments.

Amendment ¹ added (%)	Initial Soil TNT Level (mg/kg) ²				
	0	1000 spike	2000 spike	1000 cut	2000 cut
0 W 0 A	4.22	0.00\$	0.00\$	0.00\$	0.00\$
5 W 0 A	4.16	3.60*	1.40\$	3.73*	2.63*
5 W 5 A	4.54	4.23*	2.86*	4.17*	3.99*
10 W 0 A	4.26	4.03*	3.08*	3.49*	2.81*
10 W 10 A	4.29	4.03*	2.37*	4.74*	3.53*
20 W 0 A	3.18	3.71*	3.81*	3.47*	2.97*

LSD(0.1)=1.92

\$ = Significantly different from zero TNT treatment.

* = Significantly different than no amendment.

¹ Number indicates % (by dry weight) of wheat straw (W) or alfalfa (A) mixed with the soil.

² Spike designates uncontaminated soils spiked with TNT and cut designates highly contaminated field soils mixed with uncontaminated soil to achieve the desired initial TNT level.

significantly different from plants with similar amendments that were not exposed to TNT. Visual ratings of plants grown on spiked soils was similar to that of cut soils. Total dry-matter accumulation for the four harvests over 90 days is given in Table 5. Total dry matter for the plants grown in pots spiked with 1000 mg/kg was not significantly different than the same amendments without the addition of TNT, except where no amendments were added. Without amendments, dry matter accumulation was less than one-half of the control where 1000 mg/kg TNT was added to the soil. For the 1000 mg/kg cut soils, total dry matter production was less than for the spike soils. This implies plants were less tolerant where naturally contaminated soils were mixed with uncontaminated soil than where uncontaminated soils were spiked with crystalline TNT. In contrast to alfalfa, sorghum/sudangrass was able to survive in these soils where no amendments were added although harvested dry matter was drastically reduced. At the 2000 mg/kg TNT level, dry matter accumulation was less than 5% of the control and the plants would likely die with time. There was considerable variation, typical of greenhouse studies, resulting in a larger than desired least significant difference. Part of the variation was the result of poor regrowth after clipping in some pots where the growing point may have been damaged by clipping too close to the soil level.



Table 4. Visual ratings and plant height of sorghum/sudangrass (*Sorghum x sudanense* cv 73-804 FS) at 14 and 89 days after planting (DAP) on TNT contaminated soils with various organic amendments.

Initial Soil ¹ TNT(mg/kg)	Amendment ² (%)	---Visual Ratings---		-----Plant Height(cm)---	
		14 DAP	89 DAP	14 DAP	89 DAP
0	0 W 0 A	8.3	10.0	19.0	35.0
0	5 W 0 A	7.0	8.7	16.0	28.3
0	5 W 5 A	10.0	9.0	20.7	26.0
0	10 W 0 A	9.3	9.0	17.3	26.3
0	10 W 10 A	10.0	8.7	20.7	25.3
0	20 W 0 A	8.3	8.7	17.2	22.7
1000	0 W 0 A	4.0	9.3	6.3*	28.0
1000	5 W 0 A	6.3	10.0	13.7\$	31.3
1000	5 W 5 A	8.7	8.3	18.0\$	26.0
1000	10 W 0 A	8.7	9.3	18.3\$	25.0
1000	10 W 10 A	10.0	6.0	20.7\$	19.5
1000	20 W 0 A	9.3	8.3	17.3\$	23.3
2000	0 W 0 A	3.3	3.7	3.9*	10.2*
2000	5 W 0 A	4.7	9.3	7.8*	32.0\$
2000	5 W 5 A	7.0	8.7	14.3*\$	27.0\$
2000	10 W 0 A	8.3	9.7	16.0\$	29.3\$
2000	10 W 10 A	10.0	4.0	20.0\$	12.3
2000	20 W 0 A	9.0	8.7	18.3\$	24.3\$
1000c	0 W 0 A	4.3	5.3	6.3*	18.2*
1000c	5 W 0 A	5.0	10.0	12.0\$	32.3\$
1000c	5 W 5 A	5.3	9.7	11.7*\$	33.0\$
1000c	10 W 0 A	7.0	9.7	14.7\$	26.3
1000c	10 W 10 A	9.0	5.7	18.7\$	19.3
1000c	20 W 0 A	8.7	8.7	17.0\$	23.0
2000c	0 W 0 A	3.7	4.0	5.5*	9.3*
2000c	5 W 0 A	4.3	9.7	7.2*	36.0\$
2000c	5 W 5 A	5.0	10.0	16.3*\$	37.0\$
2000c	10 W 0 A	8.2	9.7	15.0\$	28.7\$
2000c	10 W 10 A	10.0	8.3	19.7\$	21.7
2000c	20 w 0 A	9.2	9.0	17.2\$	24.8\$

LSD(0.01) 4.25 13.42

\$ = Sig. vs no amend, same TNT level and type; * = Sig. vs no TNT, same amend level and type.

¹ Numbers followed by s are for soils spiked with TNT and numbers followed by c are for cut soils (highly contaminated field soils mixed with uncontaminated soil to achieve the desired initial TNT level).

² Number indicates % (by dry weight) of wheat straw (W) or alfalfa (A) mixed with the soil.



Table 5. Total Oven-dry weight (g/pot) for all harvests of sorghum/sudangrass (*Sorghum x sudanense* cv 73-804 FS) from TNT contaminated soils with various organic amendments.

Amendment ¹ added (%)	Initial Soil TNT Level (mg/kg) ²				
	0	1000 spike	2000 spike	1000 cut	2000 cut
0 W 0 A	8.46	3.54\$	0.22\$	0.73\$	0.32\$
5 W 0 A	6.34	7.31	1.97\$	5.45*	3.32
5 W 5 A	9.49	7.17	4.62*\$	3.95\$	3.90\$
10 W 0 A	6.44	6.79	7.06*	6.86*	6.56*
10 W 10 A	6.77	3.45	3.83	2.92\$	5.11*
20 W 0 A	5.66	6.41	8.23*	4.92*	6.56*

LSD(0.1)=3.78 \$ = Significantly different from zero TNT treatment; * = Significantly different than no amendment.

¹ Number indicates % (by dry weight) of wheat straw (W) or alfalfa (A) mixed with the soil.

² Spike designates uncontaminated soils spiked with TNT and cut designates highly contaminated field soils mixed with uncontaminated soil to achieve the desired initial TNT level.

Perennial ryegrass. Perennial ryegrass was the most tolerant of the species tested on TNT amended soils. This is consistent with an earlier screening study conducted in our laboratory. Except for the unamended soils, visual ratings for perennial ryegrass were often 8 or higher throughout the study even where soils had initial TNT levels of 2000 mg/kg (Table 6). Where TNT was added, the height of plants grown in amended soils was significantly greater than unamended soils but not significantly different from the 0 TNT treatment. Total dry-matter produced (Table 7) for the 1000 spike and 1000 cut treatments was not significantly different from the 0 TNT treatment where amendments were added. As with sorghum/sudangrass, plants were able to survive even where no amendment was added, but growth was drastically reduced. When compared to the 0 TNT treatment total dry matter production was also significantly less at the 2000 mg/kg spike and/or cut levels for the following treatments: 5% wheat straw, 5% wheat straw and 5% alfalfa, and 10% wheat straw. The 10% wheat straw and 10% alfalfa amendment resulted in the highest dry matter accumulation. This treatment may have resulted in more available nitrogen although all pots were treated with commercial fertilizer.

Soils Results. Residual TNT levels in each pot were measured at the termination of the experiment (Table 8). Without the addition of amendments the amount of TNT remaining after 90 days of plant growth ranged from an average of about 15% of the initial level for the 1000 spike to 60% for the 2000 cut soils. The amount extractable from the cut soils was slightly higher than for the spike soils at the 1000 mg/kg initial level and considerably higher at the 2000

Table 6. Visual ratings and plant height of perennial ryegrass (*Lolium perenne* cv Manhattan II) at 14 and 89 days after planting (DAP) on TNT contaminated soils with various organic amendments.

Initial Soil ¹ TNT(mg/kg)	Amendment ² (%)	---Visual Ratings---		----Plant Height(cm)----	
		14 DAP	89 DAP	14 DAP	89 DAP
0	0 W 0 A	10.0	10.0	6.7	15.2
0	5 W 0 A	9.3	9.3	7.0	15.7
0	5 W 5 A	9.7	10.0	7.3	16.3
0	10 W 0 A	8.7	9.7	6.5	16.3
0	10 W 10 A	10.0	10.0	8.3\$	15.7
0	20 W 0 A	9.2	8.3	6.5	14.0
1000s	0 W 0 A	3.3	2.3	1.9*	3.7*
1000s	5 W 0 A	8.7	7.7	6.8\$	14.3\$
1000s	5 W 5 A	8.3	9.0	7.2\$	15.3\$
1000s	10 W 0 A	10.0	8.0	7.8*\$	13.2\$
1000s	10 W 10 A	10.0	8.0	7.7\$	14.3\$
1000s	20 W 0 A	9.3	6.7	7.7*\$	11.5\$
2000s	0 W 0 A	4.0	2.0	2.2*	2.9*
2000s	5 W 0 A	8.0	6.7	5.5*\$	11.5\$
2000s	5 W 5 A	9.7	9.0	8.2*\$	14.0\$
2000s	10 W 0 A	8.8	7.3	7.2\$	12.7\$
2000s	10 W 10 A	9.7	9.7	7.3\$	15.8\$
2000s	20 W 0 A	10.0	9.0	8.0*\$	15.0\$
1000c	0 W 0 A	5.0	2.3	3.7*	3.1*
1000c	5 W 0 A	9.7	9.0	8.3*\$	15.0\$
1000c	5 W 5 A	10.0	9.0	9.2*\$	14.7\$
1000c	10 W 0 A	9.8	10.0	8.2*\$	15.2\$
1000c	10 W 10 A	10.0	9.7	8.0\$	15.5\$
1000c	20 W 0 A	10.0	9.3	7.8*\$	15.3\$
2000c	0 W 0 A	4.3	2.3	2.7*	3.7*
2000c	5 W 0 A	8.3	8.3	7.2\$	15.2\$
2000c	5 W 5 A	10.0	9.3	8.8*\$	15.0\$
2000c	10 W 0 A	10.0	9.0	7.8*\$	14.7\$
2000c	10 W 10 A	10.0	10.0	8.7\$	16.2\$
2000c	20 W 0 A	10.0	9.7	8.8*\$	15.0\$

LSD(0.01) 1.04 4.30

\$ = Sig. vs no amend, same TNT level and type; * = Sig. vs no TNT, same amend level and type.

¹ Numbers followed by s are for soils spiked with TNT and numbers followed by c are for cut soils (highly contaminated field soils mixed with uncontaminated soil to achieve the desired initial TNT level).

² Number indicates % (by dry weight) of wheat straw (W) or alfalfa (A) mixed with the soil.



Table 7. Total oven-dry weight (g/pot) for all harvests of perennial ryegrass (*Lolium perenne* cv Manhattan II) from TNT contaminated soils with various organic amendments.

Amendment ¹ added (%)	Initial Soil TNT Level (mg/kg) ²				
	0	1000 spike	2000 spike	1000 cut	2000 cut
0 W 0 A	8.03	0.14\$	0.08\$	0.42\$	0.25\$
5 W 0 A	6.41	5.10*	2.43\$	6.38*	3.64*\$
5 W 5 A	9.13	8.15*	5.55*\$	8.23*	5.86*\$
10 W 0 A	8.55	6.35*	5.58*\$	6.78*	5.30*\$
10 W 10 A	9.78	7.96*	7.45*	9.32*	8.75*
20 W 0 A	6.12	5.36*	5.70*	6.89*	6.24*

LSD(0.1)=2.48 \$ = Significantly different from zero TNT treatment. * = Significantly different than no amendment.

¹ Number indicates % (by dry weight) of wheat straw (W) or alfalfa (A) mixed with the soil.

² Spike designates uncontaminated soils spiked with TNT and cut designates highly contaminated field soils mixed with uncontaminated soil to achieve the desired initial TNT level.

mg/kg level at the final sampling date. The addition of all amendment combinations reduced the extractable soil TNT at the end of the experiment for the 1000 spike treatment to less than 1% of that added initially.

Since the literature and other experiments in our laboratory show very limited plant uptake, the disappearance of TNT from the soil is likely a reaction of TNT with soil organic matter. The addition of organic amendments clearly enhances the disappearance of TNT in soils. It must be pointed out that the cut soils were prepared from highly contaminated soils (approximately 20,000 mg/kg) so they were diluted approximately 10:1 and 20:1 to achieve the 2000 and 1000 mg/kg levels, respectively. Whether or not the rate of TNT disappearance would have been similar in a field soil containing similar levels of TNT that had not been mixed with uncontaminated soil is not known. We speculate, however, that recovery from a soil that had reached a field equilibrium of 1000 or 2000 mg/kg would have been higher than from the cut or spiked soils used in these experiments. Even at the 2000 mg/kg cut level in these experiments the addition of amendments resulted in less than 10% of the initial TNT level at the termination of the experiment.

A relative rate of soil disappearance can be seen in Table 9. This shows recoveries at five different sampling dates from pots where no plants were grown. Treatments seven through twelve are for soils prepared for the 1000 mg/kg initial spike treatment. Some variation in measured levels may be the result of a single sample taken from the bulk soil because of

Table 8. TNT Remaining in soil after final harvest as a percentage of TNT added.

Trt. #	Amend(%)	TNT added	Alfalfa	Ryegrass	Sorghum
			TNT Remaining (% of initial)		
1	0 W 0 A	0	0	0	0
2	5 W 0 A	0	0	0	0
3	5 W 5 A	0	0	0	0
4	10 W 0 A	0	0	0	0
5	10 W 10 A	0	0	0	0
6	20 W 0 A	0	0	0	0
7	0 W 0 A	1000 spike	20.1	11.0	13.5
8	5 W 0 A	1000 spike	0.47	0.47	0.56
9	5 W 5 A	1000 spike	0.35	0.47	0.23
10	10 W 0 A	1000 spike	0.84	0.34	0.34
11	10 W 10 A	1000 spike	0.10	0.10	0.10
12	20 W 0 A	1000 spike	0.20	0.39	0.10
13	0 W 0 A	2000 spike	36.5	35.2	34.9
14	5 W 0 A	2000 spike	1.82	0.71	0.76
15	5 W 5 A	2000 spike	0.12	0.16	0.12
16	10 W 0 A	2000 spike	0.30	0.36	0.25
17	10 W 10 A	2000 spike	0.09	0.23	0.09
18	20 W 0 A	2000 spike	0.19	0.09	0.09
19	0 W 0 A	1000 cut	21.7	20.1	17.1
20	5 W 0 A	1000 cut	3.85	14.1	4.12
21	5 W 5 A	1000 cut	4.03	1.43	7.90
22	10 W 0 A	1000 cut	4.01	4.88	2.06
23	10 W 10 A	1000 cut	1.61	23.3	1.04
24	20 W 0 A	1000 cut	13.1	3.72	2.85
25	0 W 0 A	2000 cut	61.0	61.6	57.1
26	5 W 0 A	2000 cut	8.32	8.08	7.16
27	5 W 5 A	2000 cut	4.14	2.59	6.00
28	10 W 0 A	2000 cut	7.93	13.7	7.13
29	10 W 10 A	2000 cut	2.54	3.48	6.69
30	20 W 0 A	2000 cut	3.50	6.20	2.95

W = wheat; A = alfalfa



Table 9. TNT (mg/kg) remaining in soils from control plots (no crop planted) with Days after TNT Treatment.

Amendment ¹	Trt # ²	TNT added (mg/kg)	Days after treatment				
			15	29	43	71	91
			-----Soil TNT (mg/kg)-----				
0 W 0 A	7s	1000	949	900	600	200	95
5 W 0 A	8s	1000	40	9	6	0	2
5 W 5 A	9s	1000	17	6	2	2	5
10 W 0 A	10s	1000	27	5	3	2	1
10 W 10 A	11s	1000	4	6	2	2	1
20 W 0 A	12s	1000	8	4	3	2	2
0 W 0 A	13s	2000	1,720	1,600	900	350	912
5 W 0 A	14s	2000	535	400	131	50	17
5 W 5 A	15s	2000	114	61	15	14	8
10 W 0 A	16s	2000	570	10	12	5	5
10 W 10 A	17s	2000	44	25	19	8	5
20 W 0 A	18s	2000	74	6	14	4	4
0 W 0 A	19c	1000	839	900	380	100	218
5 W 0 A	20c	1000	470	400	70	50	21
5 W 5 A	21c	1000	69	63	11	5	4
10 W 0 A	22c	1000	76	7	6	12	6
10 W 10 A	23c	1000	147	43	20	4	1
20 W 0 A	24c	1000	1,236	70	260	3	3
0 W 0 A	25c	2000	1,985	800	1,010	1,000	1,565
5 W 0 A	26c	2000	570	143	300	50	29
5 W 5 A	27c	2000	230	63	34	41	35
10 W 0 A	28c	2000	1,011	300	72	45	18
10 W 10 A	29c	2000	862	300	67	39	12
20 W 0 A	30c	2000	251	58	51	6	13

¹ Number indicates % (by dry weight) of wheat straw (W) or alfalfa (A). ² s=spiked soil; c=cut soil.

inadequate mixing. Within 15 days the concentrations extractable from the soils with added amendments were drastically reduced. The higher the amount of amendment the more rapid is the disappearance of the TNT. The rate of loss, however, in the nonamended soil was much slower and approximately 10% still remained at the conclusion of the experiment. This is similar to the levels found in pots with plants (Table 8). Treatments 13-18 (Table 9) represent soils with initial spike levels of 2000 mg/kg TNT. In general the higher the amount of amendment the faster the disappearance of TNT. These results are consistent with the fact that visual stress on the plants was often greatest early in the experiment, particularly where only 5% amendment was added.

Some variation in the results probably exists due to sampling variation caused by

incomplete mixing of the cut or spiked TNT into the soil. For example for treatment 26c the TNT level extracted at day 43 appeared to be lower than at day 29 or day 71. However, the trends for soil disappearance are consistent for all treatments and the final amounts left in the soil at the termination of the experiment are similar to the amounts found in soils where plants had been growing (Table 8). Disappearance from the cut soils is not as rapid nor as complete as from the spiked soils. The effect of amendments in the cut soils is, however, very significant in reducing soil extractable TNT and in improving plant growth and tolerance to TNT contaminated soils. At the 2000 mg/kg cut level the extractable TNT was much higher than for the corresponding spike level. Again some variation exists among sampling dates but recovery is much higher where no amendments were added even after 90 days in the greenhouse with periodic watering.

The effect of amendment on disappearance of TNT is summarized in Figure 1. This figure shows only the average values for % amendment whether wheat straw alone or in combination with alfalfa for soil spiked with 2000 mg/kg TNT. Clearly the extractable levels are significantly higher and the rate of disappearance significantly slower where no amendments are added.

Conclusions

Visual ratings, plant height, and dry matter production of alfalfa, sorghum-sudangrass, and perennial ryegrass were dramatically improved with the addition of wheat straw and/or alfalfa to TNT treated soils. Perennial ryegrass resulted in the most dry matter produced for the average of all treatments. A mix of ground alfalfa and wheat straw was most effective in increasing plant tolerance for this species and 20% total amendment resulted in more growth than 10% total amendment at the highest soil spiking level. Sorghum/sudangrass appeared to be more tolerant than alfalfa but not as tolerant as perennial ryegrass. Alfalfa did not survive on TNT treated soils where amendments were not added but did respond well to the addition of 10% or more total amendment.

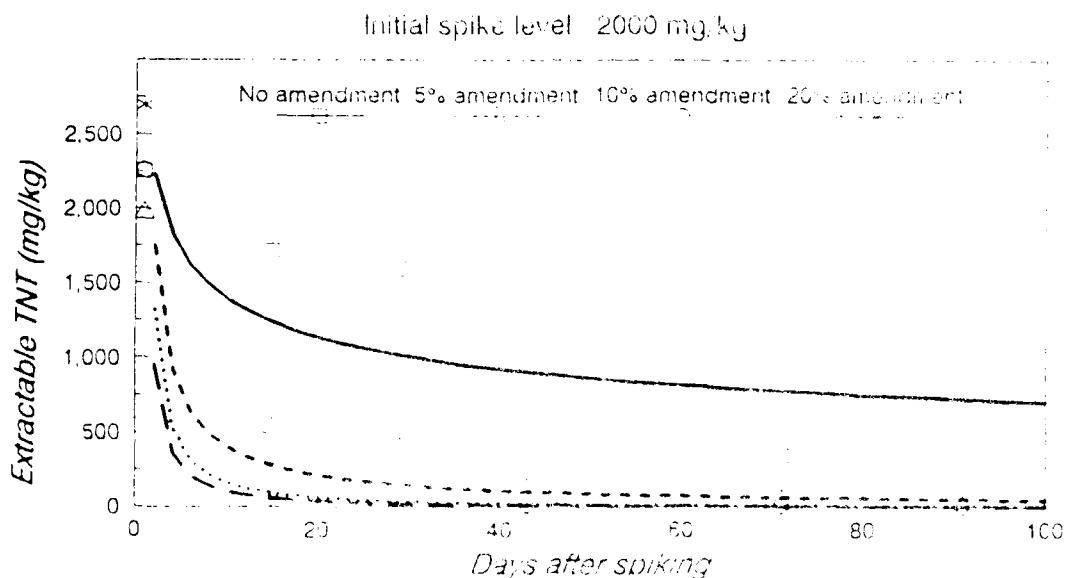


Fig. 1 Disappearance of TNT in spiked and amended soils with time (no plants)

In general the differences in plant response to amended soils was greatest in the early growth periods of the experiment. This also corresponds to higher extractable TNT levels in the soil. Plant response to soils spiked with TNT was similar to naturally contaminated soils of similar TNT level even though soils results suggest that TNT disappears more rapidly in spiked than in cut soils. Extractable TNT levels in cut soils were higher at the termination of the experiment as compared to spiked soils. Extractable levels of TNT in soils decreased rapidly with amendment level and with time.

The results of this study would imply that where field soils contaminated with TNT can be mixed with uncontaminated soil to bring the initial TNT levels to 2000 mg/kg or less and mixed with organic amendments, the probability of successful revegetation is high. This should be tested in the field.



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USE OF BIOASSAYS TO DETERMINE MIGRATION OF CHEMICAL CONTAMINATION AND SITE REMEDIATION

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ABSTRACT

The nature and extent of heavy metal contamination was assessed using plant, earthworm, and clam bioassays in conjunction with soil sample analyses. The study site consisted of terrestrial uplands, transition zones and wetlands in both freshwater and brackishwater environments contaminated with arsenic, cadmium, copper, lead, zinc, and selenium as a result of uncontrolled discharges of chemical wastes. Test data from the bioassays were used in conjunction with soil data to determine the specific areas of contamination and the need for remedial action. Laboratory plant and earthworm bioassay results and field clam bioassay results indicated potential migration of hazardous chemicals from soil into foodwebs associated with the site. Field collected small mammals confirmed bioassay test results and showed bioaccumulation of cadmium and lead in some of those areas indicated by laboratory bioassay test results. Bioassays gave a good indication of the nature and extent of chemical migration into foodwebs associated with the site.

INTRODUCTION

The evaluation of the nature and extent of heavy metal contamination in the environment and the need for remediation has become one of the most perplexing environmental challenges for mankind in recent years. This paper will describe a case study that used bioassays in conjunction with soil data to determine areas of contamination and the need for remediation (Ref 1). A Remedial Investigation was undertaken by the U. S. Department of the Navy at the Naval Weapons Station, Concord, California under the Navy Installation Restoration (IR) Program to meet requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), as amended by the Superfund Amendments and Reauthorization Act (SARA).

The investigation addressed the following questions:

1. What was the nature and extent of contamination on site?
2. Was the contamination bioavailable and migrating into foodwebs on the site?
3. What was the condition of the site and how important was the site to the natural resources of an adjacent Bay?
4. Were remedial actions required? If so, where?

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Contamination was believed to have resulted from previous uncontrolled discharges of industrial waste into environments adjacent to chemical manufacturing plants. Chemical contamination was thought to have migrated from the sources either down a creek into wetlands, or down drainage ditches in the wetlands into tidal creeks that ultimately emptied into Suisun Bay. The extent of the migration was not known in 1984, when this investigation was initiated. The entire Remedial Investigation/Feasibility Study and selection of remedial actions were completed in 1989.

OUTLINE OF STUDY AND METHODS

An experimental design for sampling the site was formulated based on previous soil and water data and the potential pathways for contaminant mobility. The site was approximately 124 hectares including a freshwater creek that flowed from rolling hills down through pastures, along side a chemical processing plant, under railroad tracks, through other pastures into a freshwater wetland, under another railroad trestle and into a brackishwater wetland tidal creek that emptied into Suisun Bay. Other sources of contaminant discharges included another chemical manufacturing plant adjacent to the brackishwater wetland. Two Reference areas were selected for the study, one upstream from waste discharges and the other on the shoreline of Suisun Bay, beyond the downstream path.

A total of 637 soil samples were collected from 424 locations across the site and in the reference areas. At 38 locations, triplicate soil samples were collected for chemical analysis, and for plant and earthworm bioassay tests, to enable a rigorous statistical analysis of the data. A total acid digestion was used to determine soil contaminant concentrations. Because of the diverse environments under investigation and the non-existence of the same colonizing species of plant or soil invertebrate at each sample site, a plant and an earthworm bioassay were conducted in the laboratory on field collected soil as indicators of contaminant migration from soil into foodwebs. A total of 178 plant and earthworm bioassays were performed on the collected soil. Plant and earthworm bioassay procedures were described elsewhere (Ref 2 and Ref 3, respectively). Since aquatic animals of the same species were not observed across the creeks and wetland sites, triplicate clam bioassays were performed at 33 locations across the site and in the reference areas to indicate contaminant migration from surface waters into foodwebs. Clam bioassay procedures were described elsewhere (Ref 4). After exposing plants and earthworms to soil samples from the site and the reference areas, plants and earthworms were harvested, weighed and analyzed for contaminant bioaccumulation. After exposing clams to the surface water in the field for 30 days, the clams were retrieved and analyzed for contaminant bioaccumulation.

Statistical analysis of the resulting data included analysis of variance (ANOVA) and Duncan's New Multiple Range Test.

All significant differences were obtained at $P = 0.05$.

RESULTS

Soil contents (dry weight basis) ranged up to 2,500 mg/kg for arsenic, up to 89 mg/kg for cadmium, up to 3,050 mg/kg for copper, up to 7,600 mg/kg for lead, up to 85,490 mg/kg for zinc and up to 138 mg/kg for selenium.

There were 11 and 6 soil sampling locations that were toxic to plants and earthworms, respectively. Plants bioaccumulated arsenic, cadmium, copper, and zinc at certain soil sampling locations to concentrations statistically above those exposed to soil from the Reference areas. Earthworms bioaccumulated arsenic, cadmium, copper, lead, and selenium at certain soil sampling locations. Clams also bioaccumulated arsenic, cadmium, lead, and zinc from surface waters in localized areas on site when compared to tissue concentrations observed in clams exposed in the surface waters of the two Reference areas. Small mammals were trapped and found to have bioaccumulated cadmium and lead in some of the areas where laboratory bioassay tests indicated potential migration of contaminants into foodwebs.

Areas of contamination were delineated as those areas where one or more test results for either soil, plant, earthworm, or clam concentration data were statistically higher than test results at the Reference areas and included locations of plant and earthworm toxicity. This approach was interpreted to mean that there was a 95% probability that at these locations, soil, plant, earthworm and/or clams would be observed to contain measureable increases in contaminants above those normally found in the Reference areas. Using this approach, approximately 18 hectares of the total 124 hectares was designated as contaminated and potentially requiring remediation.

A Feasibility Study of remedial action alternatives was conducted (Ref 5). Decision rules for the scope and extent of required remediation were developed (Ref 5). These rules considered potential criteria such as soil content exceeding values statistically higher than Reference areas; soil concentrations that exceeded the California Total Threshold Limit Concentration (TTLC) or Soluble Threshold Limit Concentration (STLC); and soil pH below 5.0. Much of the soil STLC exceedence data appeared to agree with soil sample locations of observed plant, earthworm, and clam contaminant bioaccumulation or death of plants and earthworms. In addition to these criteria, modifying factors of topography, presence of wetlands, presence of endangered species, source of contamination to other areas, and precedence were considered in drawing the boundaries of areas to be remediated. In sensitive environmental areas, application of a stringent cleanup criteria can trigger the environmental impacts waiver (Ref 6 and Ref 7). In such cases, it is necessary to balance the short-term adverse impacts associated with the remediation process with the long-term potential benefits of remediation.



Accordingly, the site was divided into zones of active remediation, passive remediation and monitoring. Contaminated areas were divided into active and passive remediation zones. Active remediation resulted in a positive control/treatment of contamination such as excavation of contaminated soil or liming to raise soil pH to 7.0. Passive remediation resulted in leaving the contamination in place and conducting short- and long-term intense monitoring of soil, water, and biota in the affected area. The impact of actively remediating the entire contaminated area was thought to be more severe than the impacts associated with leaving a portion of the contamination in place. Passive remediation was designed to identify problems, and if necessary, trigger future active remediation activities. A monitoring zone surrounding the contaminated area was established to evaluate the effectiveness of the remediation, and because contaminants may migrate into presently uncontaminated areas. Monitoring in this zone is less intensive than in the passive remediation zone and it is not considered a likely candidate for future active remediation. Bioassay tests will be conducted as part of the monitoring plan for site remediation. Based on the results of the Remedial Investigation/Feasibility Study, the total area of 124 hectares was divided into 8 hectares of active remediation, 10 hectares of passive remediation and 106 hectares of monitoring zone.

ACKNOWLEDGEMENTS

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ENDANGERMENT ASSESSMENT TECHNIQUES FOR BIOTA AT ROCKY MOUNTAIN ARSENAL

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Rocky Mountain Arsenal (RMA) is a 27 square mile parcel located east of Commerce City, Colorado. Established in 1942, RMA was a site for the manufacture and demilitarization of chemical and incendiary munitions and the manufacture of industrial chemicals, primarily pesticides and herbicides. As early as 1951, a link was suspected between waterfowl mortality at RMA and insecticide contamination of the lakes located there. In 1954 and 1955 severe crop losses were experienced by farms located north of and downgradient of RMA. Since 1974, a number of chemicals have been detected in offpost groundwater, beginning with diisopropylmethylphosphonate (DIMP), a manufacturing byproduct of the nerve agent Sarin or GB, dicyclopentadiene (DCPD) a chemical intermediate used in pesticide production, and dibromochloropropane (DBCP), a nematocide produced at RMA. Since 1978, as many as 35 chemicals have been found to be elevated in offpost groundwater. By virtue of being elevated with respect to background, they qualified as chemicals of concern according to EPA guidance (EPA, 1989).

In addition to groundwater contamination, chemicals of concern have been detected in offpost surface water of First Creek including: arsenic, aldrin, dieldrin, p,p, DDT (DDT), p,p DDE (DDE), chlordane, DCPD and DIMP. First Creek sediments also contain the following chemicals of concern: aldrin, dieldrin, DBCP, endrin DDT, DDE. Soils in the area immediately adjacent to the north boundary contain the following chemicals of concern: aldrin, dieldrin, endrin, chlordane, DDT and DDE. EPA guidance (EPA, 1989) requires that the upper 95 percent confidence limit be established for exposure point concentrations when monitoring data are used



to estimate exposures. Table 1 contains selected exposure point concentrations for carcinogenic chemicals of concern in study area three of the Offpost Operable Unit (OOU).

The offpost operable unit was established with boundaries of East 80th Avenue and the South Platte River to the west and north, Second Creek to the east and the northern boundary of RMA to the south, Figure 1. The operable unit contains about 25 square miles and is characterized as predominantly rural agricultural land uses with some industrial and residential land uses in the south and southwest portions of the OOU. Due to the spatial distribution of contaminants and the size and complexity of the OOU, the OOU was divided into six study areas, Figure 1. Study area three contained the most extensive number of chemicals of concern, contaminated media and greatest exposure concentrations, hence it is the focus of the human food chain aspects of this paper.

The primary field crops grown in the OOU are winter wheat, hay, barley, corn, sugar beets alfalfa and oats. Some areas of the OOU are irrigated from water brought into the study area and others areas rely on dryland farming. Pasture for cattle and other livestock is also significant in the area. Some feedlot operations are present. In addition, some hobby or subsistence farmers maintain small numbers of livestock for dairy, beef and poultry consumption.

Two major ecosystems occur in the OOU: terrestrial and wetland/aquatic. The physiography of the area is characterized by stream-valley lowlands and gently rolling uplands, resulting in well-defined surface water drainages with riparian habitat, few relatively wetland features and large expanses of dryland prairie features. The surface water features include the intermittent streams First and Second Creeks, which arise at RMA flowing generally in a northwesterly direction toward the South Platte River. In addition, several irrigation canals traverse the OOU from west to east discharging in Barr Lake, a State of Colorado park and wildlife refuge. Barr Lake is the most important aquatic habitat in the OOU; it is stocked with warmwater fish species for recreational fishing and for wildlife species which include white pelicans, great blue herons, cormorants, egrets, ducks, grebes, owls, eagles and hawks. In addition to the presence of a large heron rookery, a pair of bald eagles has nested at Barr Lake since 1986. Terrestrial ecosystems

have been significantly disturbed by agricultural use and include weedy forbs and grasses habitats and fencerows that sustain wildlife species of limited diversity. Prairie dogs, deer mice, pheasants are most numerous prey species for the bald and golden eagles, hawks (e.g. American kestrel) and owls (e.g. great-horned owl); other predators include red fox, coyote, skunks and raccoons. White-tailed and mule deer are also found in the study area (HLA, 1991a).

EXPOSURE PATHWAYS

The pathways evaluated by the endangerment assessment included human food chain and ecological food web pathways, in addition to dermal, inhalation and ingestion of water, soil and sediment. The focus of this paper are those pathways involving the biota.

Human Food Chain

The human portion of the endangerment assessment considered a residential scenario that included agricultural components. This was considered to be the reasonable maximum exposure (RME) scenario where a hobby or subsistence farmer lived in the contaminated area and grew and consumed most of his own food products.

The human food chain pathways consisted of human consumption of locally produced dairy products, beef, eggs and crops. Each of these was subdivided by the contribution afforded by surface water (irrigation), groundwater (irrigation) and soil. Exposure intake equations were derived according to EPA guidance (EPA, 1989, 1990) and according to equilibrium partition coefficient theory as described by Rosenblatt (1975), Baes et al (1984), Briggs et al (1982, 1983) and Kenaga (1980). Typical intake equations contain the exposure factors as arranged as in the following examples for the soil contribution to human chronic daily intake (CDI) of:

$$\text{Crops: } \text{CDI} = C_s \cdot (k_{sr} \cdot \text{IR}_r \cdot k_{sp} + \text{IR}_p) \cdot \text{EF} \cdot \text{ED} / \text{BW} \cdot \text{AT} \quad (1)$$

$$\text{Dairy: } \text{CDI} = C_s \cdot [\text{IR}_d \cdot k_{pd} \cdot (k_{sp} + I_{ps})] \cdot \text{EF} \cdot \text{ED} / \text{BW} \cdot \text{AT} \quad (2)$$

$$\text{Beef: } \text{CDI} = C_s \cdot [\text{IR}_m \cdot k_{pm} \cdot (k_{sp} + I_{ps})] \cdot \text{EF} \cdot \text{ED} / \text{BW} \cdot \text{AT} \quad (3)$$

$$\text{Eggs: } \text{CDI} = C_s \cdot \text{IR}_e \cdot k_{se} \cdot \text{EF} \cdot \text{ED} / \text{BW} \cdot \text{AT} \quad (4)$$

where: CDI = human chronic daily intake in mg/kg/day; C_s = soil concentration; EF = exposure frequency (days/yr); ED = exposure duration (30 years); BW = body weight (70 kg); AT = averaging time (days/lifetime). Selected exposure intake parameters are shown in Table 2. Similar intake equations were prepared for groundwater and surface water contributions to the crop, dairy and beef pathways. A complete listing of intake equations and exposure factors, values and references is quite lengthy and may be obtained by writing the author. Dimensionless partition coefficients were obtained from the technical literature, while more generic exposure factors (e.g. IR, EF, ED, BW, AT) were taken from EPA guidance (EPA, 1989, 1990, 1991).

A Latin hypercube uncertainty analysis was performed on the human food chain intake equations to better understand the distribution of the concentration range predicted from distribution of the partition coefficients for dieldrin in plants, eggs and meat. In addition, limited site-specific sampling results for cow tissue were available for comparison. Figure 2 shows the results of this analysis. The projected meat dieldrin concentrations are plotted versus the cumulative probability in percent. Table 3 summarizes the results for plants, eggs and meat. The 50th percentile is the mean estimate, while EPA guidance recommends use of the 95th percentile. The table shows the 50th percentile, the 95th percentile and the point estimate of the RME calculation used in the exposure assessment. It may be seen from Table 3 and Figure 2 that the RME actually falls around the 98th to 99th percentiles of the distribution. The actual sampling results are also plotted on Figure 2 with an arrow marked "D", and fall between the 38-65th percentile. Hence, it was concluded that the RME used is slightly more conservative than EPA's recommendation.

While the focus of this paper is on the biota aspects of the endangerment assessment, a number of other human exposure pathways were also quantified. The contribution to exposure and risk from the human food chain pathways relative to the other pathways will be presented. The other pathways quantified included: dermal exposure to surface water, dermal exposure to sediments, dermal exposure to soils, domestic use of groundwater (ingestion and showering), ingestion of soils and ingestion of sediments.

Ecological Assessment

The ecological assessment addressed the ecosystems described previously, terrestrial and aquatic; in addition an agri-ecosystem was evaluated to assess potential threat to the agricultural products (crops and livestock) inherent to their own health. Simplified food webs were constructed and indicator species were identified at each trophic level, Figures 3, 4 and 5. Indicator species selection was based on the following criteria: (1) species observed or collected in the OOU, (2) species is an important component of offpost food chains, (3) species is a rare, threatened or endangered species known to occur onpost or offpost, (4) species is an important commercial or sport species, (5) species is of high public interest, (6) species fills trophic niche in simplified food web, (6) sensitivity to chemicals of concern, (7) availability of ecotoxicity data for related taxa.

The most important chemicals of ecological concern were required to be present in concentrations exceeding background in soil, surface water or sediment, and were required to have significant ecological effects, (e.g. high bioaccumulative potential based on log octanol-water partition coefficients). The following were selected from the chemicals of concern for the affected media to be considered in the ecological assessment: aldrin, dieldrin, endrin, arsenic, DDE and DDE. Each of these chemicals has the ability to bioaccumulate in the food web. Inasmuch as carnivorous birds are the most conspicuous predators in the OOU, the food webs featured bald eagles, great-horned owls and American kestrels at the top of the terrestrial food web, bald eagles and great-blue herons at the top to the aquatic food web, and livestock at the top of the agricultural food web.

The ecological endpoint for the to be evaluated for the terrestrial ecosystem was the predicted tissue concentration of the chemical in the receptor species at the top of the respective food web. Other ecological endpoints such as population diversity were not considered due to the confounding effects of human disturbance in the OOU. This predicted tissue concentration (PTC) was compared with the maximum allowable tissue concentration (MATC) derived from the literature. A model was developed by Fordham et al (1991) that utilized bioaccumulation factors (BAFs) multiplied together for the various terrestrial exposure pathways in the model. Further

development of the input parameters was performed by Ebasco (1991). Each exposure pathway was assigned a fraction of the receptor species diet. For example, the owl pathways included: soil>worm>mouse>owl; soil>plant>insect>mouse>owl; soil>plant>insect>owl; and soil>plant>mouse>owl. Table 4 shows the bioaccumulation factors by pathway for the ecological chemicals of concern. The product of the chemical-specific BAFs times the dietary fractions results in a weighted BAF for the owl. Table 4 also shows the total BAFs for the target species, by chemical of concern.

The MATC is estimated from the toxicity reference value (TRV) derived in the toxicity assessment (HLA, 1991b) as follows:

$$\text{MATC (ug/kg)} = \text{TRV (ug/kg)} * \text{BAF} \quad (5)$$

MATC values were extrapolated from other animal data when species-specific data were unavailable in the literature reviewed. MATC reflects the maximum tissue concentration below which toxic effects would not be expected.

RISK CHARACTERIZATION

This section presents some of the preliminary results of the endangerment assessment with an emphasis on the chemicals of concern and exposure pathways that contribute significant risk.

Human Food Chain

For human food chain exposures, the chronic daily intakes were multiplied times carcinogenic slope factors obtained from EPA data bases to obtain pathway carcinogenic risks. Similarly, EPA reference doses were used to obtain noncarcinogenic hazard indices in accordance with EPA guidance (EPA, 1989). Since the carcinogenic chemicals tend to create the lowest risk-based remedial criteria, only the exposure and risk results for carcinogens are described. Carcinogens contributing to total risk included: aldrin, arsenic, atrazine, benzene, chlordane, chloroform, DDE, DDT, DBCP, 1,2 dichloroethane, dieldrin, tetrachloroethene and trichloroethene. In addition, only the results from study area three are presented due to space limitations.

Figure 6 summarizes the excess cancer risk contributed by arsenic, dieldrin, DBCP and chloroform via the food chain pathways in comparison to the other exposure pathways (HLA, 1991b). It may be seen that the organochlorine pesticides contributed the majority of the exposure via the food chain, outweighing drinking water ingestion, soil ingestion and other non-food chain intakes, whereas chemicals such as arsenic, chloroform and DBCP, which do not bioaccumulate as significantly, contributed relatively much less exposure via the food chain. Figure 7 shows the total excess cancer risk for all carcinogens in study area three. It may be seen that vegetable and dairy product consumption are the two primary exposure pathways, and that when combined with the egg and meat pathways, contribute about 75 percent of the total risk. Aldrin and dieldrin contributed 78 percent of the excess cancer risk, DBCP contributed 9.6 percent of the excess cancer risk and arsenic contributed 7.4 percent of the cancer risk.

A quantitative uncertainty analysis is planned for DIMP, dieldrin, chloroform and arsenic, but has not been completed. It will feature probability plots of the risk distribution, in conjunction with the RME point estimate of risk.

Preliminary risk-based remedial action criteria will be computed by rearranging the exposure intake equations using a 10^{-6} risk-based reference dose and back-calculating to safe media (groundwater, surface water, soil and sediment) concentrations.

Ecological Assessment

Table 5 presents preliminary results for the terrestrial food web models. Table 5 shows the predicted tissue concentration for the target species. This was obtained by multiplying the soil concentration times the weighted BAFs for each target species. These predicted concentrations are compared with the MATC for the target species. At the time of writing these have only been derived for bald eagles. The results indicate exceedences for DDT and dieldrin. However, inasmuch as bald eagles have a very large home range with respect to study area three (approximately 200 acres), this exceedence may not warrant remediation based on ecological effects alone. Remedial action criteria will be computed by using the food web model maximum allowable tissue concentrations to back-calculate allowable soil concentrations.

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TABLE 1. Selected Exposure Point Concentrations, Study Area 3, Upper 95% Limit,

Chemical	Ground Water ug/l	Surface Water ug/l	Soil ug/kg	Sediment ug/kg
arsenic	2.2	17.7	0	0
aldrin	0.25	0	14	11
atrazine	4.7	0	0	0
carbon tetrachloride	0	0	0	0
chloroform	3.1	0	0	0
chlordane	0.83	0.18	115	0
DBCP	0.46	0	0	10
DDE	0.27	0.09	45	0.5
DDT	0	0.05	171	8
1,2 dichloroethane	1.24	0	0	0
dieldrin	0.72	2.6	134	134
endrin	0.56	0	179	4
trichloroethene	0.89	0	0	0
tetrachloroethene	7.1	0	0	0

TABLE 2. Identification of Exposure Parameters, Food Chain Pathways

Cs, Cgw, Csw	Concentration in media		
kpd	PC: plant/dairy	IRr	Human ingestion rate roots
kwp	PC: water/plant	IRI	Human ingestion rate leafy
kpm	PC: plant/meat	IRd	Human ingestion rate dairy
kwp	PC: water/plant	IRm	Human ingestion rate meat
kwr	PC: water/root	IRe	Human ingestion rate eggs
fE	plant fraction exposed	lpwd	Intake of water, dairy cow
kdep	PC: deposition/plant	lpwm	Intake of water, beef cow
ksr	PC: soil/root	lps	Intake of soil, cow
ksp	PC: soil/plant	GWF	crop irrigation fraction from gw
kse	PC: soil/egg	1-GWF	crop irrigation fraction from sw

TABLE 3. Uncertainty Analysis Results, Dieldrin Food Chain Pathways, ug/kg

Pathway	50th %	95th%	RME	RME%
Plants	0.028	0.064	0.082	98.7
Eggs	0.013	0.026	0.039	99.5
Meat	0.012	0.021	0.032	98.8

TABLE 4. Terrestrial Bioaccumulation Factors by Pathway, RMA Offpost OU

Pathway	Aldrin	Arsenic	DDE	DDT	Dieldrin	Endrin
s>w>m>o,k	36.3	0.55	25.2	25.2	15.2	17.4
s>p>i>m>o,k	55.6	0.01	224.8	710.5	55.6	97.5
s>p>i>o,k	52.9	0.01	68.3	216	53	12.8
s>p>m>o,k	2.1	0.15	7	22.1	2.1	3.4
s>p>ph>e	18.6	0.13	46	145.5	18.6	3.5
s>p>pd>e	0.32	0.15	7	22	3.6	3.3
s>p>i>ph>e	491	0.01	1482	4687	491.5	101.4

Total BMF for Target Species for Food Web

Species	Aldrin	Arsenic	DDE	DDT	Dieldrin	Endrin
kestrel	42.9	0.05	80.4	253.4	42.8	42
owl	30.4	0.1	106	333.6	29.9	92
eagle	9.4	0.01	28.2	89.2	9.5	2

TABLE 5. Predicted (PTC) vs Maximum Allowable Tissue Concentrations (MATC), ug/kg

Species	Aldrin	Arsenic	DDE	DDT	Dieldrin	Endrin
kestrel PTC	227.8	176.4	1808	3142	1342	4304
owl PTC	162	387	2387	4136	939	9424
eagle PTC	50	36	636	1106	299	209
eagle MATC	267	ND	1239	101	267	1310

ND-Not determined at this time

Note: Other MATC not determined at this time



cm3dirmc

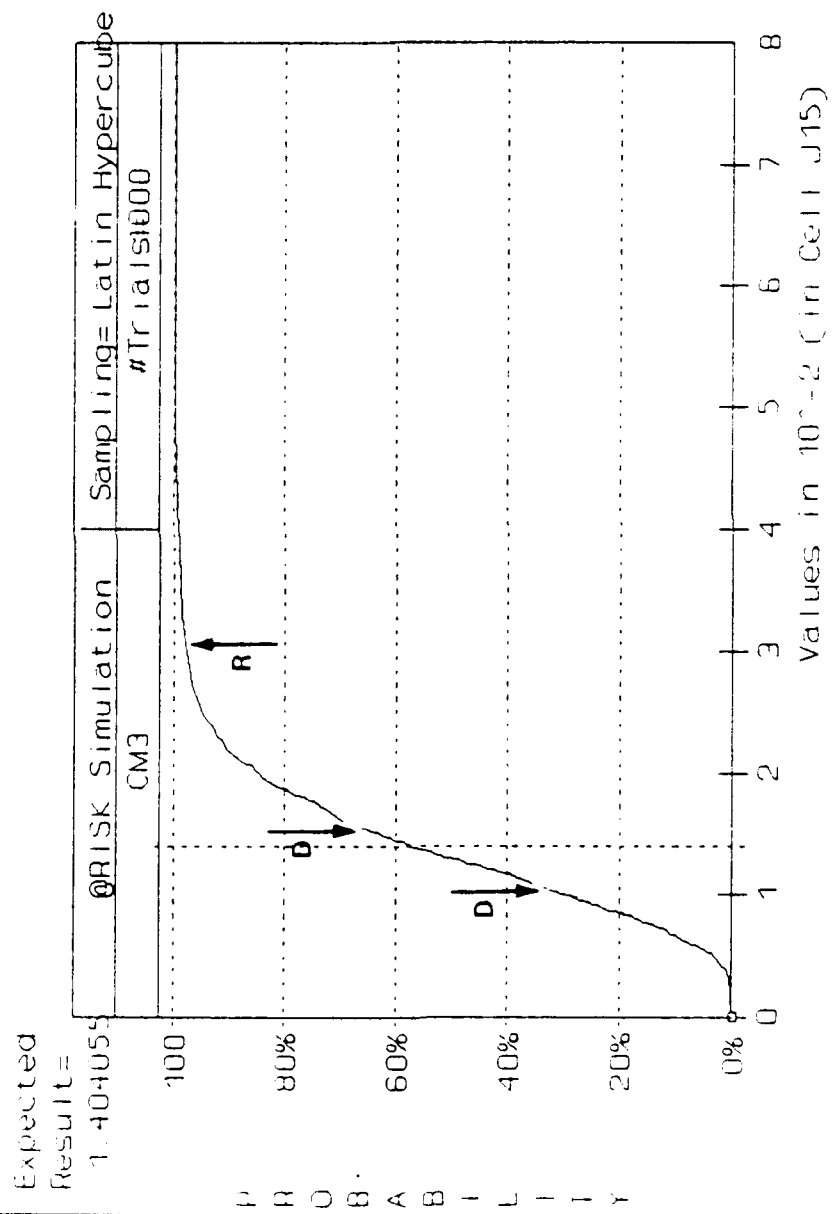


Figure 2.

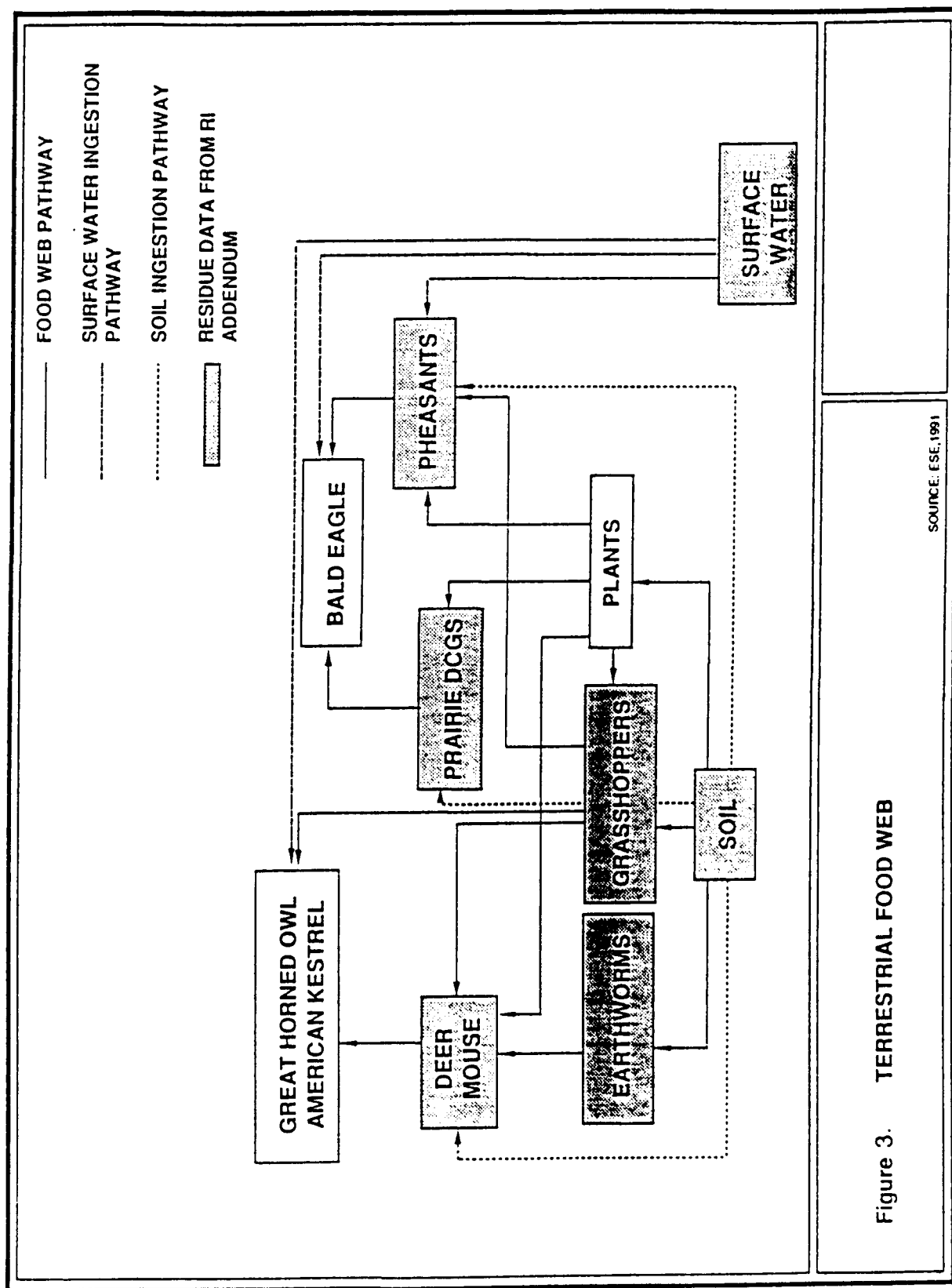


Figure 3. TERRESTRIAL FOOD WEB

SOURCE: ESE, 1991

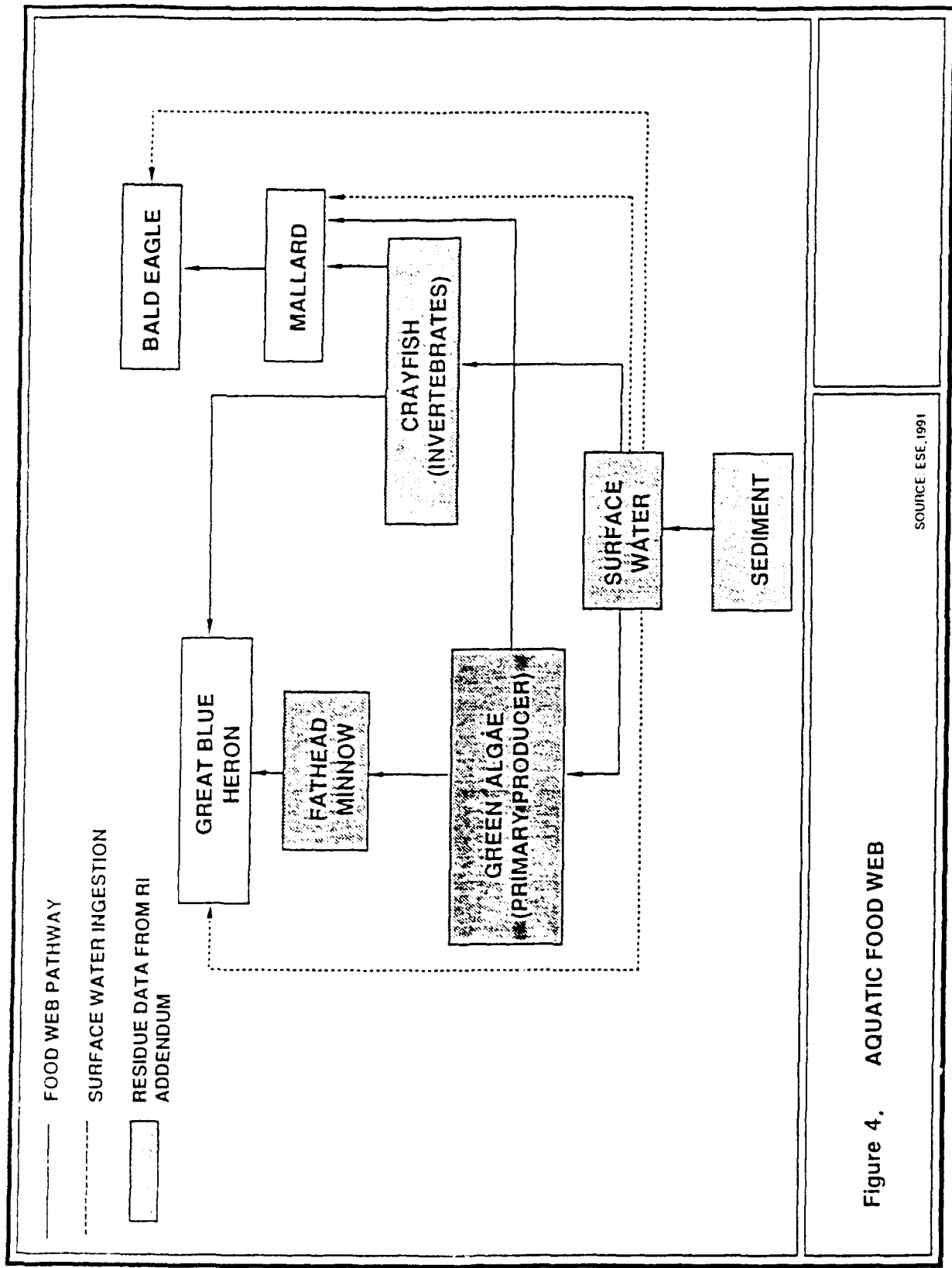


Figure 4. AQUATIC FOOD WEB

SOURCE: ESE, 1991

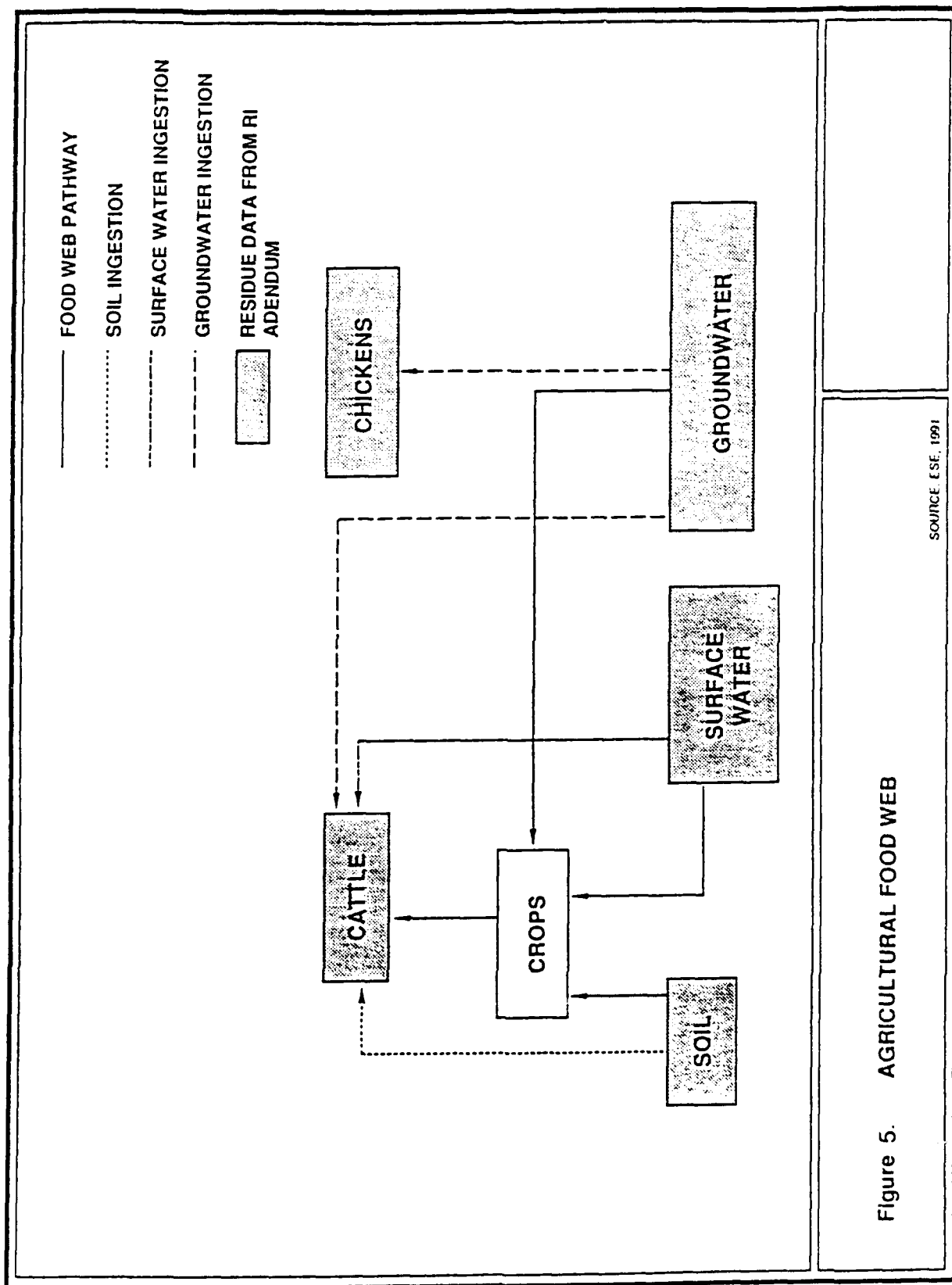


Figure 5. AGRICULTURAL FOOD WEB

SOURCE: ESE, 1991

FIGURE 6. RMA OFFPOST OU EXCESS CANCER RISK BY PATHWAY

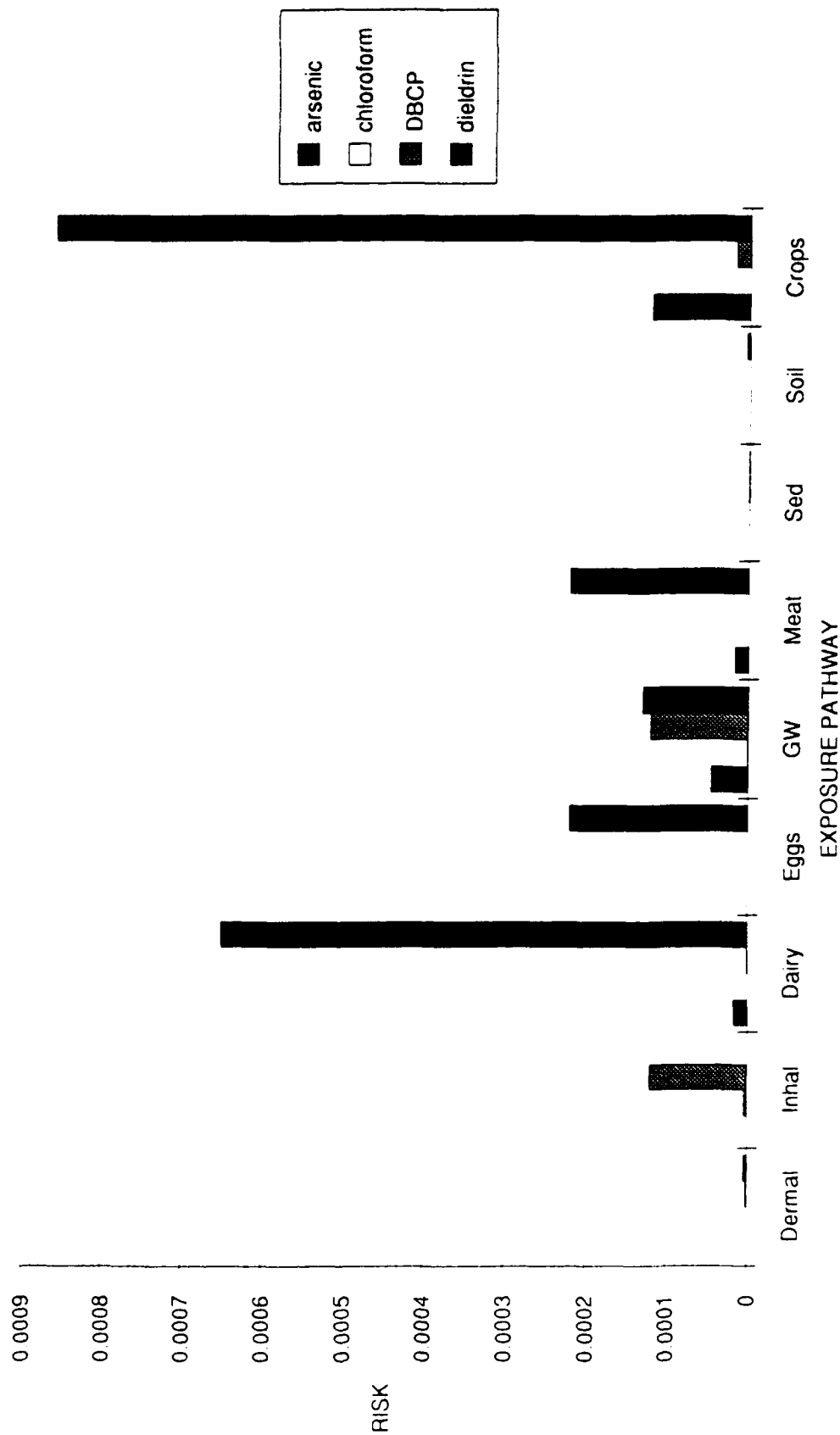
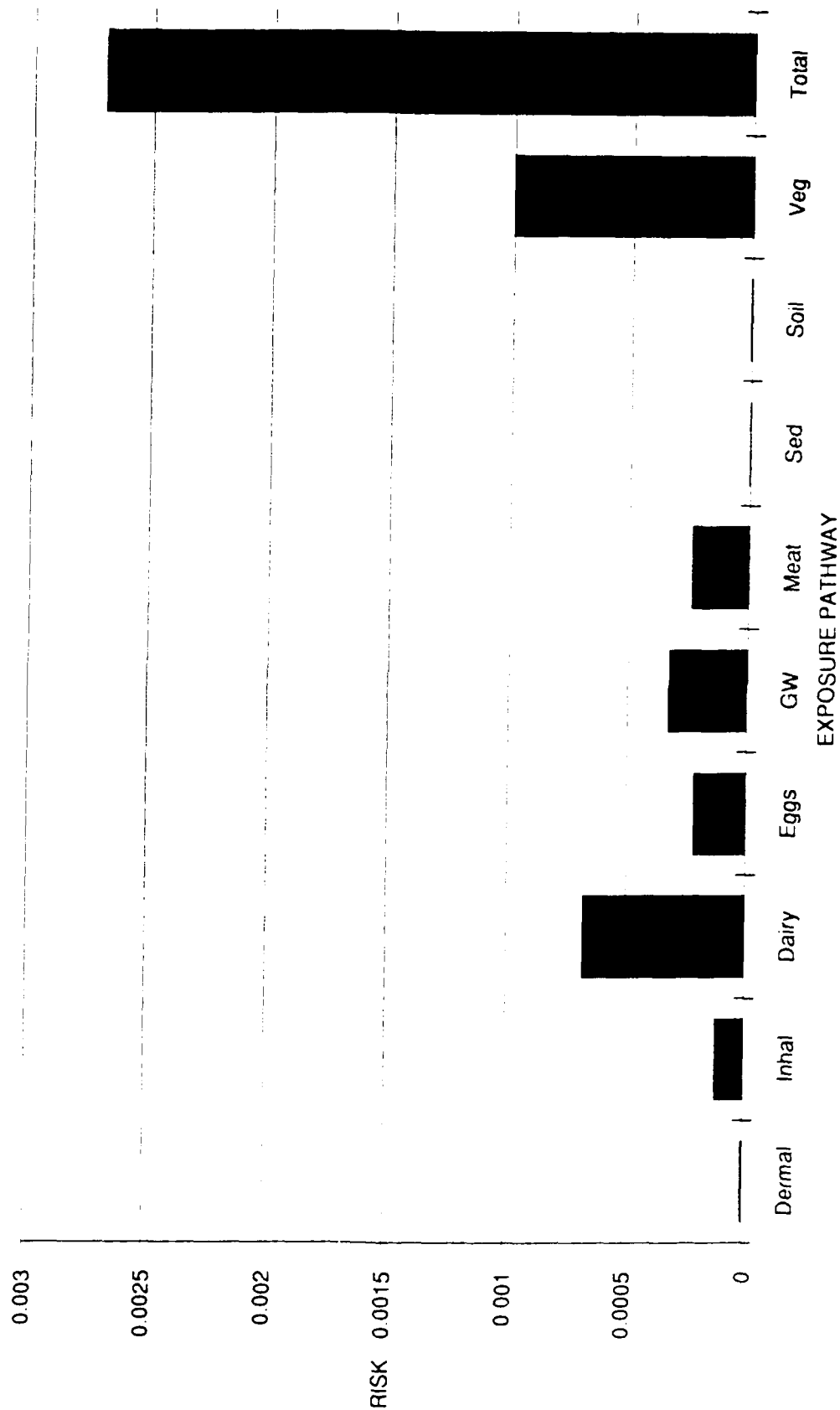


FIGURE 7. RMA OFFPOST TOTAL CANCER RISK, STUDY AREA 3





TNT METABOLITES IN ANIMAL TISSUES FROM US ARMY AMMUNITION SITE

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I. INTRODUCTION

1. Background

Regulatory agencies have recommended that tissue of deer living in TNT-contaminated areas of the former *Alabama Army Ammunition Plant (AAAP)* site at Childersburg, AL be analyzed to ensure that they are free of excessive toxic contamination resulting from ingestion of contaminated soil, water and plant materials. The potential compounds of concern are the parent compound 2,4,6-trinitrotoluene (TNT); 2,4-diamino-6-nitrotoluene (2,4-DA-6-NT); 2,6-diamino-4-nitrotoluene (2,6-DA-4-NT); 2-amino-4,6-dinitrotoluene (2A-4,6-DNT); 4-amino-2,6-dinitrotoluene (4A-2,6-DNT); 2,4,6-trinitrobenzyl alcohol (TNB alcohol); 2,4,6-trinitrobenzoic acid (TNB acid); 1,3,5-trinitrobenzene (TNB); 4-hydroxylamino-2,6-dinitrotoluene (4HOA-2,6-DNT); 2-hydroxylamino-4,6-dinitrotoluene (2HOA-4,6-DNT); and 2,6,2',6'-tetranitro-4,4'-azoxytoluene (Azoxydimer). These compounds were identified (El-hawari, et al. 1981) in the urine of various small animals after administration of TNT. The chemical structure and possible route of metabolic formation are detailed in Figure 1. The study design criterion level for total concentration of TNT and metabolites had been established as 1.2 mg/kg in animal flesh (Rosenblatt, personal communication). In setting this level, Rosenblatt assumed that all involved compounds were comparable in toxicity to TNT and used plausible estimates of the average daily intake of venison by exposed individuals. Thus, the design analytical sensitivity goal for any of the individual compounds was 0.1 milligrams per kilogram of flesh.

2. Project Aims

The overall objectives of this study were to: (1) provide quantitative analytical procedures for the analysis of TNT and related metabolites at a level of 0.1 milligram per kilogram of tissue



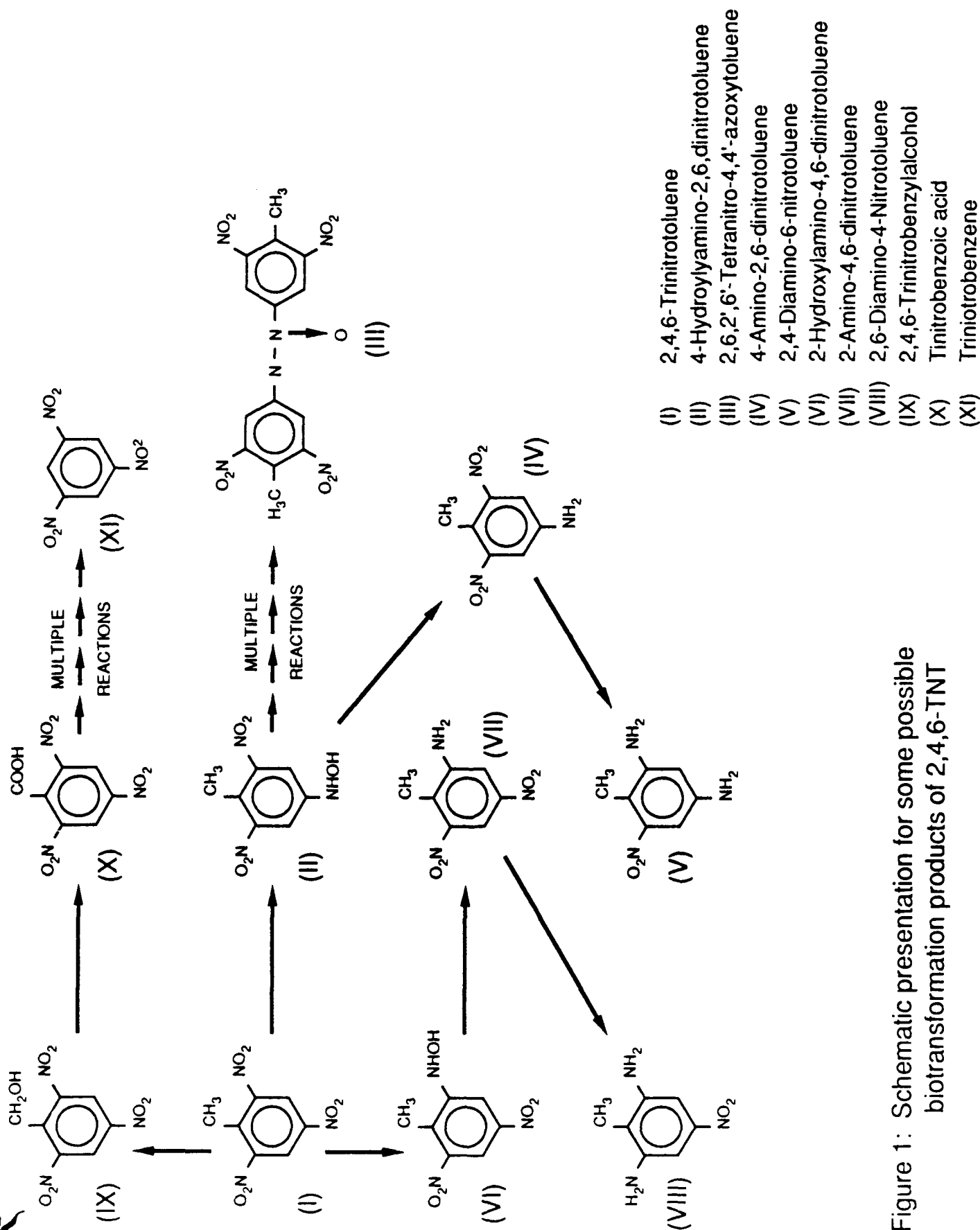


Figure 1: Schematic presentation for some possible biotransformation products of 2,4,6-TNT

or less for each compound; and (2) obtain representative samples of tissues from several species of animals (deer, rabbit, and quail) at the AAAP site in Childersburg, AL and to determine the presence or absence of TNT and its metabolites in these samples.

3. Experimental Approach

To meet the overall objectives of this project, the following individual tasks were identified:

Task 1 - Develop analytical procedures for the detection and quantification of the TNT and related compounds.

Task 2 - Demonstrate the extractability of all the TNT-compounds from "spiked" animal tissue at an analytical sensitivity of 0.1 mg/kg/metabolite.

Task 3 - Obtain tissue from deer, rabbit, and quail at the AAAP site and analyze each sample for TNT-compounds following procedures developed in Tasks 1, 2, and 3.

Task 4 - Present a Statistical Design for sampling and analysis of deer tissue.

II. EXPERIMENTAL METHODS

1. Procedures for the Analytical Detection of TNT and Metabolites

Previous workers (e.g., Kaplan and Kaplan 1982; Yinon and Hwang 1985; and Elhawari, et al. 1981) have used both reverse phase and normal phase HPLC to separate TNT and certain of its metabolites. We tested these and other reverse phase HPLC methods but were not able to satisfactorily resolve all the compounds required for this study. A separation and detection procedure for TNT and its possible metabolites was successfully developed using a mixed-mode HPLC. The HPLC column (Alltech Associates, Inc., 150 mm X 4.6 mm i.d.; 5 micron particle size; Cat. No. 72620) stationary phase bonded to the silica surface contains both a C18, (reversed-phase function) and a secondary amine, (anion exchange function) incorporated into a single ligand in a 1:1 ratio. The separation utilizes a gradient built from three different eluting solvents: A. an aqueous solution containing phosphate that has been adjusted to pH 5.1 with the final concentration of phosphate being 0.015 M in a 10:90 water:methanol solvent; B. methanol; and C. acetonitrile. The sources of phosphate are potassium dihydrogen phosphate and dipotassium hydrogen phosphate in the appropriate amounts to achieve the desired pH and concentration. Control of pH with the buffer is crucial to achieving the necessary separation. The gradient program starts with equilibration at 72% Solvent A and 28% acetonitrile and elution with this mixture for 1 min after sample injection. From 1 to 5 min a linear gradient reduces solvent A from 72% to 68% and increases acetonitrile from 28% to 32%. Isocratic elution conditions are then maintained for the time interval from 5 to 14 minutes. Between 14 and 20 min a linear gradient reduces solvent A by 4% per minute and increases both methanol and acetonitrile by 2% per minute so that at 20 min the eluting solution is 44% solvent A, 12% methanol and 44% acetonitrile. From 20 to 26 min a linear gradient reduces solvent A from 44% to 2% and increases methanol from 12% to 54% while maintaining the acetonitrile at 44%. Isocratic conditions are then maintained from 26 to 33 min. Then between 33 and 38 min a very steep gradient restores the eluting solution to its starting conditions after which the column is re-equilibrated for 7 min.



For analysis, a 50- μ L aliquot of a sample is injected onto the column maintained at ambient temperature and eluted at a flow rate of 1 mL per min. Detection is at 254 nm with a Hewlett-Packard 1090 Liquid Chromatograph equipped with a diode array UV detection, automatic sampling system, and Chem Station data system. The instrument was calibrated using eight different concentrations of TNT and metabolites over the range of 0.1 through 5 PPM in solution.

2. Extraction Procedure for the Recovery of TNT and Metabolites from Animal Tissue

An extraction procedure for the isolation and recovery of TNT and metabolites from animal tissue was developed using samples spiked with known amounts of TNT-related compounds. The procedure was as follows:

- (i) Thaw tissue (1.96 - 2.04 g) on ice and mince. Transfer to centrifuge tube.
- (ii) Add 6 mLs of CH_3CN (note: all organic solvents are pretreated with Na_2SO_4 before use) and homogenize with a "Polytron" (3X, 200 watts, ~ 15 sec).
- (iii) Remove debris by centrifugation (Sorvall Superspeed RC2-b; 10 min, 0°C ; 3000 rpm) and rewash pellet with 6 mLs CH_3CN , repeat centrifugation, combine supernatants, and take to dryness with N_2 .
- (iv) Resuspend dried extract in 2 mLs H_2O by shaking for 1 min then transfer to separatory funnel. Add 5 mLs CHCl_3 and mix phases by shaking (50X). Recover CHCl_3 phase and re-extract H_2O phase with 5 mLs CHCl_3 . Combine CH_3Cl phases, add 1 g of Na_2SO_4 and mix by vortexing. Recover CHCl_3 , take to dryness with N_2 , resuspend in 100 μL CH_3OH , and store at 4°C .

3. Statistical Analysis

A statistical design with the objective of deciding whether a chemical and its metabolites are likely to be present in the tissues of an animal population at or above a designated criterion level when only a portion of the population has been sampled was formulated (Beauchamp, et al. 1991). In the absence of such compounds in sampled animals at the detection level, the statistics are designed to quantify the confidence concerning absence of excessive contamination at the criterion level in the remaining population. In this regard, supplementary data analysis was provided (Shugart, et al. 1991) to support the assumption that the magnitude of σ (standard distribution of a chemical in an exposed animal) can be described by a lognormal distribution.

III. RESULTS

1. Extraction of Animal Tissues

Recovery data for deer liver tissue that was spiked with 1.25 ppm each of TNT-related compounds is tabulated in Table 1. The liver tissue was obtained from nonmunition-contaminated deer at the Catoosa Wildlife Management Area in East Tennessee spiked in the laboratory with 1.25 ppm each of the compounds listed in Table 1 and extracted according to the standardized protocol (see Section II.2). The extract was analyzed by the mixed-mode HPLC method (see Section II.1).



Table 1. CORRECTED RECOVERIES OF TNT-RELATED COMPOUNDS
FROM SPIKED DEER LIVER TISSUE.

Compound ^a	% Recovery
	\pm s.d. (n=3)
TNT (I)	84.0 \pm 4.3
TNB (XI)	76.0 \pm 10.6
2,4-DA-6-NT (V)	53.3 \pm 6.1
2,6-DA-4-NT (VIII)	41.0 \pm 4.4
4A-2,6-DNT (IV)	111.6 \pm 4.0
2A-4,6-DNT (VII)	113.3 \pm 6.0
4HOA-2,6-DNT (II)	3.6 \pm 10.0
TNB alcohol (IX)	103.3 \pm 7.8
TNB acid (X)	9.3 \pm 12.5
Azoxydimer (III)	4.3 \pm 1.5
DNB (surrogate standard)	100 ^b

^a Roman numeral refers to designation noted in Figure 1.

^b Absolute recovery was 56.7 \pm 3.2%

2. Development of Analytical HPLC Procedures

An example of the separation of a standard mixture in acetonitrile containing 1 ppm (each) of TNT and metabolites by the mixed-mode HPLC method is shown in Figure 2. The total gradient program required 45 min to complete, including a final 7-min re-equilibration period at the end of the program.

3. Collection and Analysis of Animal Tissues from Field Sites.

a. Field Collection Activities.

(1). Control Sites. Control samples of muscle and liver tissue from deer, rabbit and quail were obtained from nonmunition-contaminated animals. These animals were collected on the Oak Ridge National Laboratory reservation or at the Catoosa Wildlife Management Area in East Tennessee from January through August of 1989. The collection was under the supervision of personnel from the State of Tennessee Wildlife Resources Agency and all tissue collected were archived under liquid nitrogen at the Oak Ridge National Laboratory.

(2). AAAP Site. Animals were hunted on the Alabama Army Ammunition Plant site, Childersburg, AL from Sunday, November 26, 1989 through Tuesday, December 5, 1989. An accurate record of all samples was kept and a chain of custody maintained. All samples collected were archived at the Oak Ridge National Laboratory under liquid nitrogen and under lock and key. The inventory from this hunt include: liver and muscle tissue from 12 deer, 5 quail, and 5 rabbit.



MIXED MODE HPLC OF STANDARDS

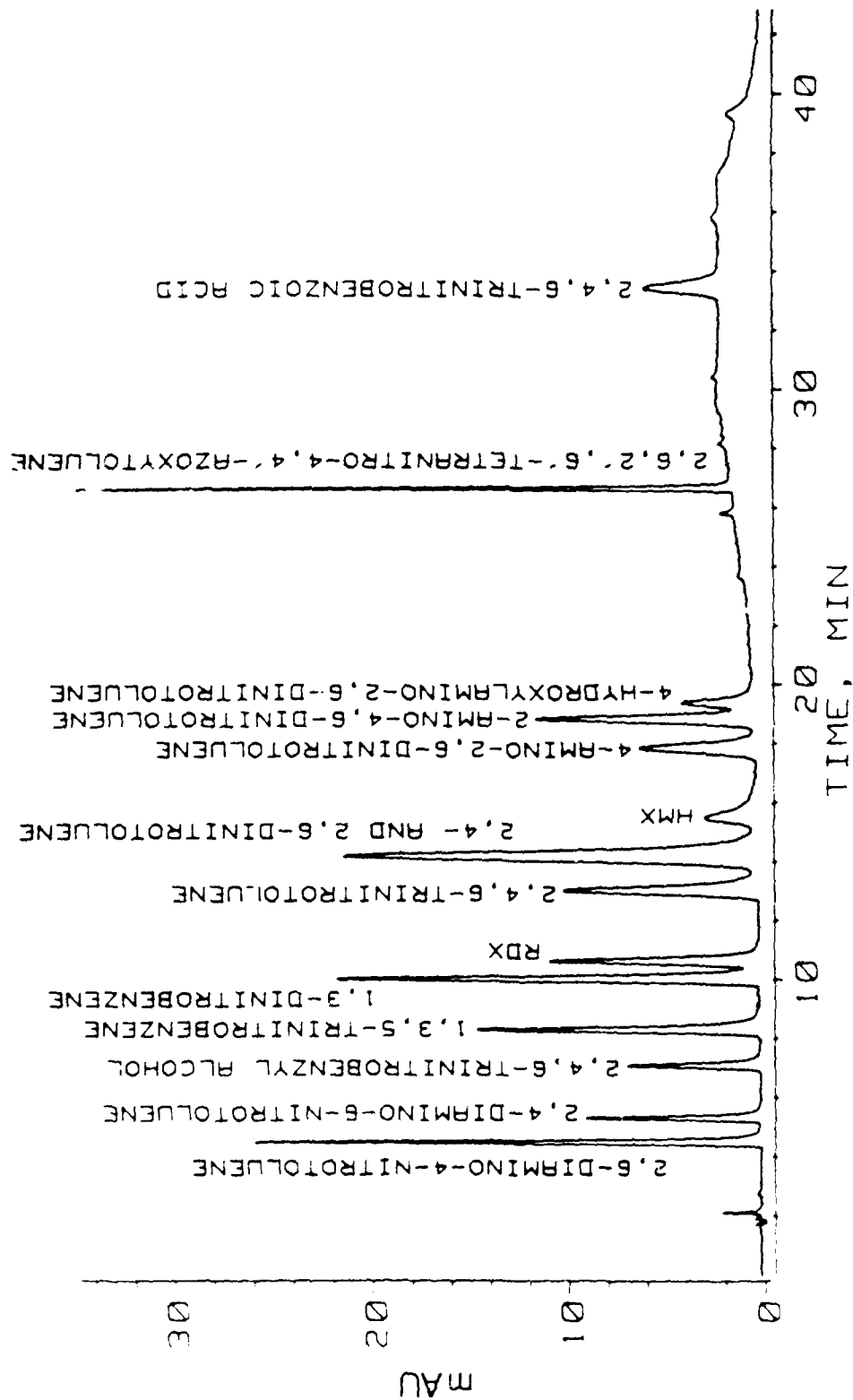


Fig. 2. Chromatographic Separation of Authentic TNT and Metabolites by Anion/C18 Mixed-Mode Column.

b. Sample Analyses

A total of 168 separate analyses were performed on the various field-collected animal tissues to determine whether TNT-related chemicals were present. The number and type of samples processed are listed in Table 2. Each analysis consisted of the extraction of an individual tissue (or blank) sample followed by HPLC on a mixed-mode column and examination of the eluent for TNT and its metabolites.

TABLE 2. NUMBER AND TYPE OF FIELD-COLLECTED SAMPLES PROCESSED FOR TNT-RELATED CHEMICALS

Sample Type	Samples ^a	Controls ^b	Spikes ^c	Total
Deer Liver	36(12)	5	11	52
Deer Muscle	36(12)	3	3	42
Rabbit Liver	12 (4)	6	0	18
Rabbit Muscle	15 (5)	6	1	22
Quail Liver	7 (5)	2	0	9
Quail Muscle	15 (5)	5	2	22
Blank (no tissue)			3	3
Totals	121	27	20	168

- ^a Samples indicate number of tissue preparations analyzed from the AAAP site. Number in parenthesis indicates the number of animals from which these samples were derived.
- ^b Controls refer to processed tissue samples from animals taken from a non-contaminated site.
- ^c Spikes refer to processed samples to which known amounts of several metabolites were added before processing.

IV. DISCUSSION/CONCLUSIONS

1. Extraction Procedure

The following factors were considered paramount for the development of the extraction procedure adopted:

- Enrichment of those compounds of interest with a minimum co-extraction of extraneous matter.
- Acceptable and reproducible recoveries of spiked authentic compounds.
- Recovery of those compounds of interest in a matrix compatible with the analytical HPLC techniques used for detection and quantification.

The data in Table 1 indicate that overall the recovery and reproducibility was very good and that the extraction method performed well for the parent compound TNT, the monoaminodinitro metabolites, TNB alcohol, and TNB. Experiments showed that only the

azoxydimer was sensitive to the nitrogen blow-down. The more polar diaminomononitro metabolites are extracted to a lesser extent, but recovery is satisfactory. TNB acid, 4HOA-2,6-DNT, and the azoxydimer are poorly recovered and the following specific problems dealing with chemical stability of these compounds were noted:

- (i) TNB acid decomposes very quickly in acetonitrile. In fact, a freshly prepared solution of TNB acid in acetonitrile begins to show significant amounts of TNB and no TNB acid can be observed after 24 hours at ambient temperature. Decomposition begins immediately in 1:1 acetonitrile:water but proceeds more slowly. In aqueous solution TNB acid appears to be stable for an extended period of time. This observation may present some problems for the metabolite determination in tissue. In aqueous media such as tissue TNB acid would be stable; however, extraction of the metabolites from the tissue requires the use of an organic solvent in which any TBA would decarboxylate. Thus the analyzed sample may show TNB while the tissue initially contained some TNB acid.
- (ii) The second stability problem concerns 4HOA-2,6-DNT which decomposes to the azoxydimer under the solvent conditions used for HPLC. This decomposition is observed immediately in a freshly prepared solution and proceeds slowly over an extended period of a week or more until the 4-HOA-2,6-DNT is no longer observed. Dependency of this instability on different solvent media has not been observed.
- (iii) Finally, the azoxydimer demonstrates an instability attributable to photosensitivity.

2. HPLC Methodology

The detection limits for TNT and metabolites using the mixed-mode (anion/C18) HPLC method have been determined according to the procedure discussed by Hubaux and Vos, (1970), and are listed in Table 3. Limits are presented for two different confidence levels. These limits represent the amount of compound that would be detected in animal tissue if two grams of tissue were extracted into a final volume of 0.5 mL with 50 μ L of this extract then being analyzed. The data listed in Table 3 and the chromatogram shown in Figure 2 were generated from sample volumes of 50 μ L, and thus they represent a realistic expectation for this method. More ideal results have been generated by injecting standards in volumes of 10 μ L or less. Thus the method described yields very good results for most compounds even though a sample volume that is 5 or more times the ideal is injected. The HPLC procedure also is capable of detecting the explosives HMX and RDX if they are present above the Hubaux-Vos detection limits, but the instrument was not routinely calibrated for those explosives because they were not observed in the samples.



Table 3. CHROMATOGRAPHIC PARAMETERS FOR EXPLOSIVES AND TNT METABOLITES ON MIXED MODE ANION/C18 COLUMN

COMPOUND	RET. TIME, MIN.	K ^a	SYM ^b MIN.	DET. LIMIT ^c 95, 99, PPM PPM	
1,3,5-TRINITROBENZOIC ACID	34.0	17.3	1.3	0.07	0.10
2,4-DIAMINO-6-NITROTOLUENE	5.7	2.1	1.1	0.09	0.12
2,6-DIAMINO-4-NITROTOLUENE	4.8	1.6	1.3	0.03	0.04
TRINITROBENZYL ALCOHOL	7.2	3.3	0.84	0.13	0.18
RDX	11.0	4.9	0.72	0.10	0.14
HMX	14.8	7.0	1.2	0.09	0.14
1,3-DINITROBENZENE	10.1	4.5	1.2	0.05	0.07
1,3,5-TRINITROBENZENE	8.3	3.5	1.2	0.05	0.07
2-AMINO-4,6-DINITROTOLUENE	19.1	9.3	1.1	0.15	0.22
4-AMINO-2,6-DINITROTOLUENE	18.2	8.8	0.93	0.06	0.09
2,6-DINITROTOLUENE	14.4	6.8	1.1	0.15	0.20
2,4-DINITROTOLUENE	14.5	6.8	1.1	0.12	0.16
2,4,6-TRINITROTOLUENE	12.8	5.9	1.1	0.05	0.10
4-HYDROXYAMINO-2,6-DINITROTOLUENE	20.2	9.9	1.2	0.2	0.34 ^d
2,6,2',6'-TETRANITRO-4,4'-AZOXYTOLUENE	26.6	13.3	1.3	0.5	0.7

^a The K-value, (capacity ratio), is the corrected retention time divided by the time required for an unretained compound to travel through the system.

^b SYM is the total peak area after the apex divided by the total peak area before the apex.

^c DET. LIMIT is the detection limit in PPM for tissue extracts assuming two grams are extracted into a final volume of 0.5 mL with 50 μ L of this extract injected. These detection limits have been calculated for the 95 % and 99 % confidence levels according the methods suggested by Hubaux and Vos (1970).

^d The detection limits listed for 4-HOA-2,6-DNT must be considered approximations because this compound has limited stability under the chromatographic conditions employed.

3. Determination of TNT and Metabolites in Animals from AAAP Site

a. Analysis of Animal Tissues.

Of the 168 separate analyses on field-collected animal samples (Table 2), one was completely lost during filtration. The recovery standard was 1,3-dinitrobenzene (DNB), which was added to each tissue at a level of 1.25 PPM. Recoveries generally were very good: 85% (23 out of 27) of the control samples analyzed and 78% (93 out of 120) of AAAP samples analyzed showed recoveries of DNB >50%.

The recovery of different analytes varied. Compounds with greater water solubility such as 2,4-DA-6-NT and 2,6-DA-4-NT tend to have lower recoveries from the sample preparation process employed. Major interferences most often tended to be in the chromatographic region where 2,4-DA-6-NT, 2,6-Da-4-NT, and TNB alcohol eluted.

Although the determined detection limits ranged as low as 0.05 PPM for some analytes, the background contributed by the tissue preparation process tends to raise the practical detection limit to levels on the order of 0.1 PPM. None of the target analytes were present in the samples at levels greater than 0.2 PPM. Without further investigation one can not rule out the possibility that some target analytes may be present at lower levels. Reanalysis using a confirmation column with a different separating mechanism, (e.g., normal phase vs reversed phase), might reduce the background interference contribution.

b. Statistical Analysis and Significance of Data.

In the results reported in this study, none of the tissues analyzed was found to contain TNT or its metabolites above the detection limit of 0.2 PPM, therefore the following exercise was performed with the data obtained from AAAP site deer tissue (refer to Beauchamp, et al. 1991):

For a deer population size of $N = 300$; a random sample size of $n = 12$; and with zero observed number of animals with an individual metabolite concentrations greater than the detection limit (DL) of the analytical procedure used; then from Wright's Tables (Wright, 1991), we find the upper 95% confidence limit on the proportion of the population that exceeds the DL to be 0.22 (i.e., we are 95% confident that no more than 22% (65/300) of the deer population exceeds the DL for an individual compound).

This confidence statement about the proportion of the population that exceeds the DL can be converted to a confidence statement about the proportion greater than the CL if we assume the distribution of TNT-related observations are lognormal (Shugart, et al. 1991) and that $\ln CL$ is $k^*\sigma$ units above $\ln DL$. The upper limit on the proportion > DL may be converted to an upper limit on the proportion > CL, by finding the proportion of the distribution > $\mu + (0.78 + k^*)\sigma$, where the value k^* is defined as $((\ln CL - \ln DL)/\sigma)$.

For $\sigma = 0.887$ (the value for σ is taken from Shugart, et al. 1991), and CL and DL in PPM, $k^* = (\ln 1.2 - \ln 0.2)/.887 = 1.792/.887 = \underline{2.02}$

Then from standard statistical tables on the proportion of the normal curve (one-tailed) that lies beyond a given normal deviate, we can say with 95% confidence that this proportion is 0.0026. Thus, no more than 0.26% of the 300 deer exceed the CL limit, or approximately 1 deer.

An important consideration in the above exercise is the assumption concerning the magnitude of σ and that the distribution of observation of TNT-related compounds is lognormal. In this regard, these consideration were evaluated from a statistical analysis of data obtained on the high-resolution gamma-ray analyses for ^{137}Cs content in the muscle and liver tissue of road-killed deer samples at the Oak Ridge National Laboratory during the 1983 calendar year. Deer are known to come in contact with ^{137}Cs as a result of their normal drinking and browsing activities on the ORNL Reservation, similar to the type of contact anticipated for munitions-like chemicals at the AAAP site. A summary of the statistical analysis for the road-killed data and the estimation of σ , is given in Shugart, et al. 1991.

The significance of the body burden data for TNT-related compounds in rabbit and quail from the AAAP site is uncertain since a statistical analysis could not be performed as with the deer data. This was because neither an accurate population estimate of these animals at the AAAP site was available nor a documented σ value, calculated from an exposure data base that was lognormally distributed.

Nevertheless, it is encouraging that none of the tissues analyzed from the animals at the AAAP site contained TNT-related compounds above the detection limit of the method of analysis and is probably indicative of negligible environmental exposure by these species to these compounds.

V. ACKNOWLEDGEMENT

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WATERFOWL MORTALITY IN EAGLE RIVER FLATS IMPACT AREA, ANCHORAGE, ALASKA¹

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ABSTRACT

The death of hundreds of migrating dabbling ducks and 10-50 swans has been documented yearly for the last ten years in Eagle River Flats (ERF), an estuarine salt marsh on Ft. Richardson, Alaska. This marsh has been used for the past 40 years as an artillery impact range by the U.S. Army. During May and August 1990, CRREL collected over 250 sediment and water samples and analyzed them for munitions residues. We found 2,4-DNT in a limited area of ERF not used by waterfowl and white phosphorus in sediments from the bottom of shallow ponds where waterfowl feed. Tissues from waterfowl observed to die or found dead in the salt marsh were collected, and we found white phosphorus in the gizzards of all 19 carcasses collected in Eagle River Flats. Adult mallards dosed in the laboratory with white phosphorus showed identical behavioral symptoms to those of wild ducks observed to become sick and die in Eagle River Flats. All evidence indicates that white phosphorus, as a particulate in the sediments, is responsible for the death of waterfowl in Eagle River Flats. Since the bottom sediments of the shallow salt marsh ponds are anaerobic, the white phosphorus particles will persist in the sediments indefinitely and remain a threat to waterfowl.

¹ Work funded by USATHAMA, CPT Steven Bird, Project Officer.



INTRODUCTION

Every year during fall and spring migrations, hundreds of waterfowl have been found dead in Eagle River Flats (ERF), a 1000-ha estuarine salt marsh located along Cook Inlet, Alaska (Fig. 1). The cause of this unusual mortality has remained a mystery despite numerous investigations by federal and state agencies. Analyses of waterfowl carcasses recovered from Eagle River Flats by various wildlife laboratories ruled out avian diseases and lead poisoning, and analyses of sediment and water samples failed to show significant levels of any poisonous compounds or heavy metals.

Eagle River Flats, which is part of Ft. Richardson, has been used as a U.S. Army artillery impact training area into which well over 100,000 projectiles have been fired. Because a study by USATHAMA (ESE 1990) concluded that munitions are the cause of waterfowl mortality in ERF, the Commanding General, 6th Infantry Division (Light), temporarily suspended the use of ERF as an impact area in February 1990. Despite the suspension, large numbers of waterfowl have continued to die. Because of CRREL's expertise in chemical analyses for munitions residues and in Alaskan wetlands ecology, we were requested by USATHAMA to test the hypothesis that munition residues are the cause of mortality in ERF (Racine et al., in press). We conducted field studies in ERF during May and August 1990.

We based our approach to finding the waterfowl poison on four basic conditions or assumptions:

- Possible incomplete combustion and subsequent storage of munitions may occur in the standing water and saturated soils of a wetland environment;
- Because certain species of waterfowl, primarily dabbling ducks and swans, are the principal victims, the poison probably resides in sediments, which are processed by feeding waterfowl;
- Only some of the waterfowl that enter and feed in ERF die; therefore, the poison must be unevenly distributed in certain areas of this 1000-ha marsh; and
- Because waterfowl have continued to die despite the cessation of firing in February 1990, the poison is not rapidly degraded in the salt marsh sediments.

Our four major objectives during 1990 were to:

- Conduct chemical and physical analyses of sampled sediments, water and tissues of affected waterfowl;
- Describe the behavior of affected waterfowl from their first symptoms after feeding until their death;



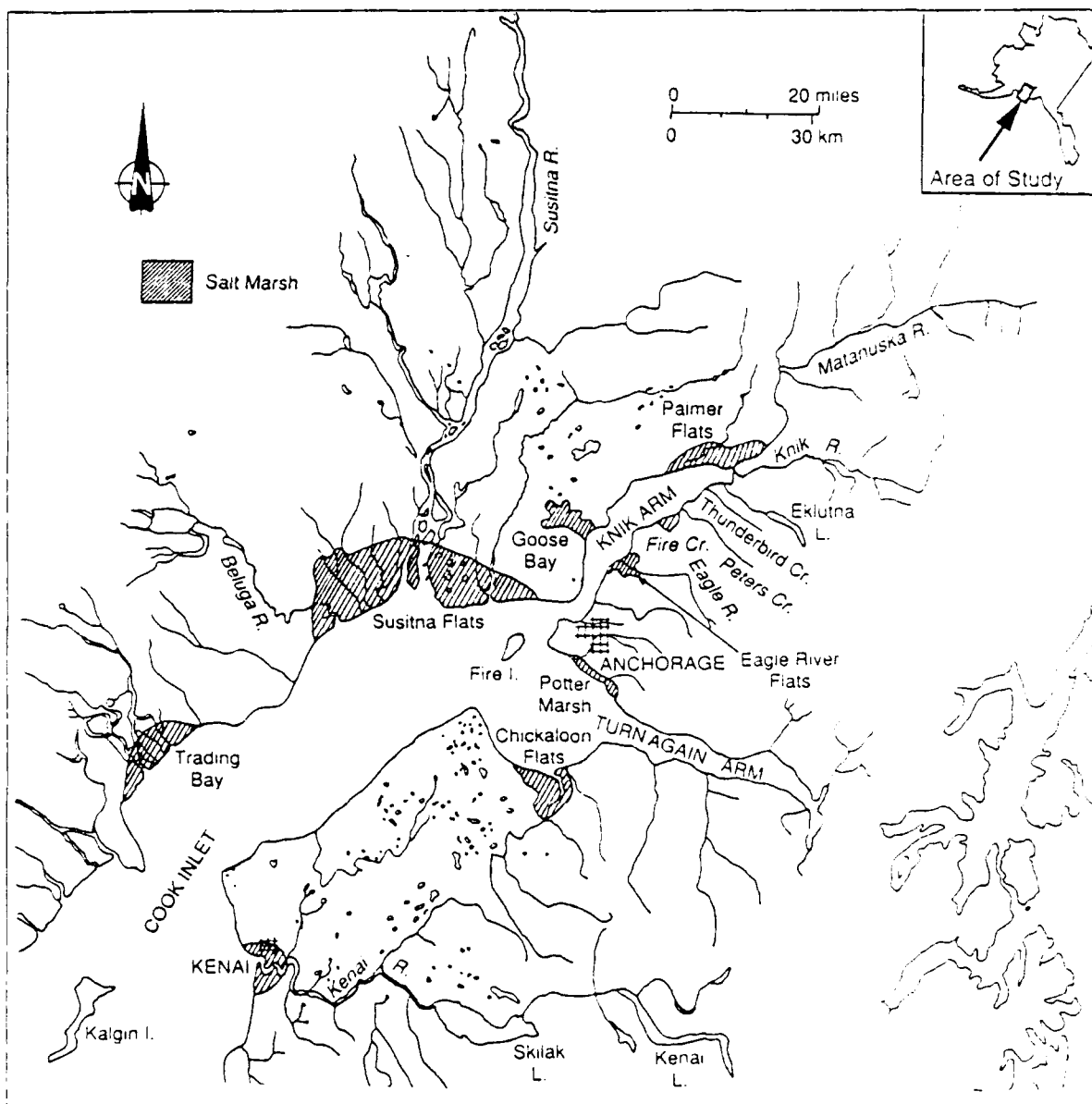


Figure 1. Location of Eagle River Flats

- Conduct laboratory experiments in which suspected chemicals are fed to domestic ducks; and
- Determine the basic environmental conditions in ERF and the military use of the area that could affect the types, location, storage or movement of munitions residues.

Records of the types of ordnance used in the impact area date back to only 1987. Based on these records, munitions used include high explosives such as RDX and

TNT, smokes (white phosphorus and hexachloroethane-zinc mixture), and illumination flares containing magnesium. Of the various munitions that have been fired into Eagle River Flats, the smoke-producing white or elemental phosphorus (P_4), became a prime suspect when a sediment sample collected in May was observed to smoke. White phosphorus is known to be highly toxic to waterfowl (Coburn et al. 1950) and other animals, including humans (Murphy 1986).

METHODS

Sampling

Salt marsh sediments were collected during waterfowl migrations in May and August 1990. The May samples were collected throughout the salt marsh, with an emphasis on areas with numerous impact craters. Based on the results of the May sampling, intensive sampling in August was conducted along the northeast edge of the salt marsh where an Explosive Ordnance Disposal (EOD) area is located. The top 5 cm of sediments were collected at each sampling point. The depth of the overlying water, as well as the pH and redox potential of each saturated sediment sample, were measured. In addition, in February 1991, frozen sediment cores were collected through the ice using an ice core auger. Over 200 sediment samples were obtained, and each collection site was precisely located by surveying so sampling sites can be easily relocated.

Analyses for munitions

Samples were analyzed for nitroaromatics (TNT, TNB, DNT) and nitramines (RDX, HMX) by field screening methods (Jenkins 1990, Walsh and Jenkins 1991) and by HPLC (Jenkins et al. 1989). Sediments with the highest concentrations of analytes were also analyzed by GCMS (gas chromatography-mass spectrometry) to provide firm confirmation of analyte presence as well as identification of some unknowns.

Sediments and waterfowl tissues were analyzed for white phosphorus by GC-FPD (gas chromatography-flame photometric detector) (Addison and Ackman 1970) and by GCMS. To identify particulate white phosphorus in the sediments, samples that tested positive for white phosphorus by GC-FPD were placed in Calgon, a dispersing agent, and then washed through a 0.150-mm mesh sieve. The material left in the sieve was placed in water and examined under a stereomicroscope for particulate white phosphorus.

Observations of waterfowl behavior

Waterfowl were observed with spotting scopes and binoculars from shore in August and from a 6-m-tall observation tower during September. When a bird became sick, it was approached and its behavior monitored carefully and recorded with both video and still cameras.

Laboratory toxicity study

Domestic mallard ducks were dosed with one of two munitions compounds: white phosphorus or 2,4-DNT. Dose levels were 10 mg/kg for white phosphorus and 1 g/kg for 2,4-DNT. The intent of the study was to compare the behavioral symptoms of laboratory ducks dosed with a known quantity of the two munitions compounds found in ERF with the behavioral symptoms of poisoned birds observed in ERF. Behavioral observations were recorded, and blood and/or tissue samples were analyzed following dosing. Blood samples from birds dosed with 2,4-DNT were analyzed for methemoglobin, a form of hemoglobin produced by 2,4-DNT. Tissue samples from birds dosed with white phosphorus were analyzed for white phosphorus.

RESULTS

Analyses for nitroaromatics and nitramines

Neither RDX nor TNT was detected in any of the 93 sediment and water samples collected in May 1990 with the field screening procedures. However, when the samples were analyzed in the laboratory by liquid chromatography, three sediment samples from the salt marsh adjacent to the EOD area were found to contain 2,4-DNT, a propellant ingredient. Subsampling of one contaminated sample revealed that the 2,4-DNT was heterogeneously distributed. The concentration varied with each subsample (0.61, 3.42, 4.82, 18.0 and 27.4 $\mu\text{g/g}$ dry wt). In addition this sample contained other compounds, including 2,6-DNT (0.03–0.89 $\mu\text{g/g}$), 2,4,6-TNT (0.15–0.50 $\mu\text{g/g}$), 2-amino-4,6-dinitrotoluene (0.08–0.47 $\mu\text{g/g}$) and 4-amino-2,6-dinitrotoluene (0.16–0.52 $\mu\text{g/g}$). The compounds 2,6-DNT and TNT are byproducts of the manufacture of 2,4-DNT for propellants and as such are present at much lower concentrations. The amino compounds are biotransformation products of TNT, which form when a nitro group on the TNT molecule is reduced.

Of the 172 samples collected from the salt marsh in August 1990, 62 were contaminated with 2,4-DNT. All of these samples were collected from along the base of, or in the salt marsh adjacent to, the EOD area. In most samples with concentrations of



2,4-DNT greater than 1 $\mu\text{g/g}$, 2,6-DNT and TNT were also confirmed but at much lower concentrations. Also present in some samples were trace amounts of 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene.

In August, propellant grains were found scattered on the EOD pad and in the adjacent salt marsh. The acetonitrile extracts of these propellant grains and the sediment samples containing the highest concentrations of 2,4-DNT were analyzed by GCMS. The mass spectra showed similar compounds in the sediments and grains, including 2,4-DNT and 2,6-DNT as well as diphenylamine and dibutylphthalate (Fig. 2). These compounds are components of M1 propellant (U.S. Army 1984).

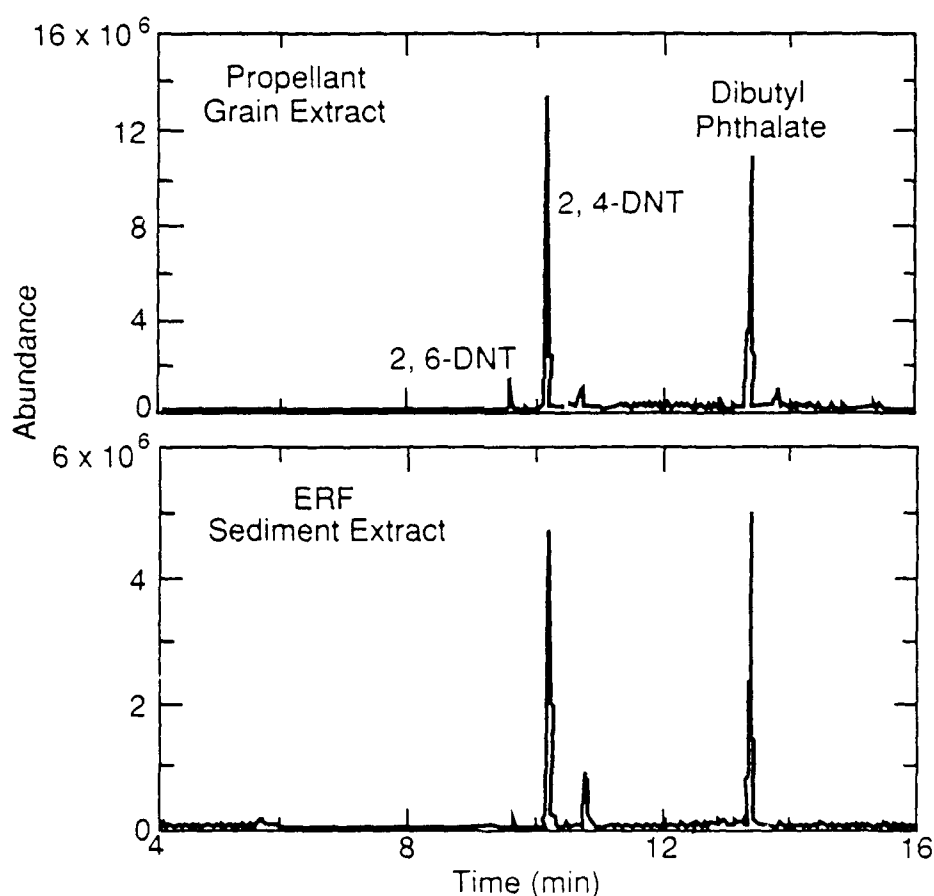


Figure 2. Gas chromatograms of a propellant grain extract and a sediment extract.

Analyses for white phosphorus in sediments

White phosphorus was determined by GC-FPD in 6 of the 20 sediment samples obtained from the shallow ponds where waterfowl were observed to become sick. Concentrations varied from 10.2 $\mu\text{g/g}$ wet weight down to 0.0025 $\mu\text{g/g}$. The presence of white phosphorus was confirmed by GCMS in the sample with 10.2 $\mu\text{g/g}$ of white



phosphorus (Fig. 3). Concentrations varied greatly in sediment subsamples from the same sample, so it is difficult to define concentrations. White phosphorus was also identified in one sample collected from an area of tall sedge near the EOD pad. This sample actually gave off a cloud of white vapor and a garlic-like odor when the sample jar was opened in the laboratory. The concentration of white phosphorus in this sample was over 1 mg/g.

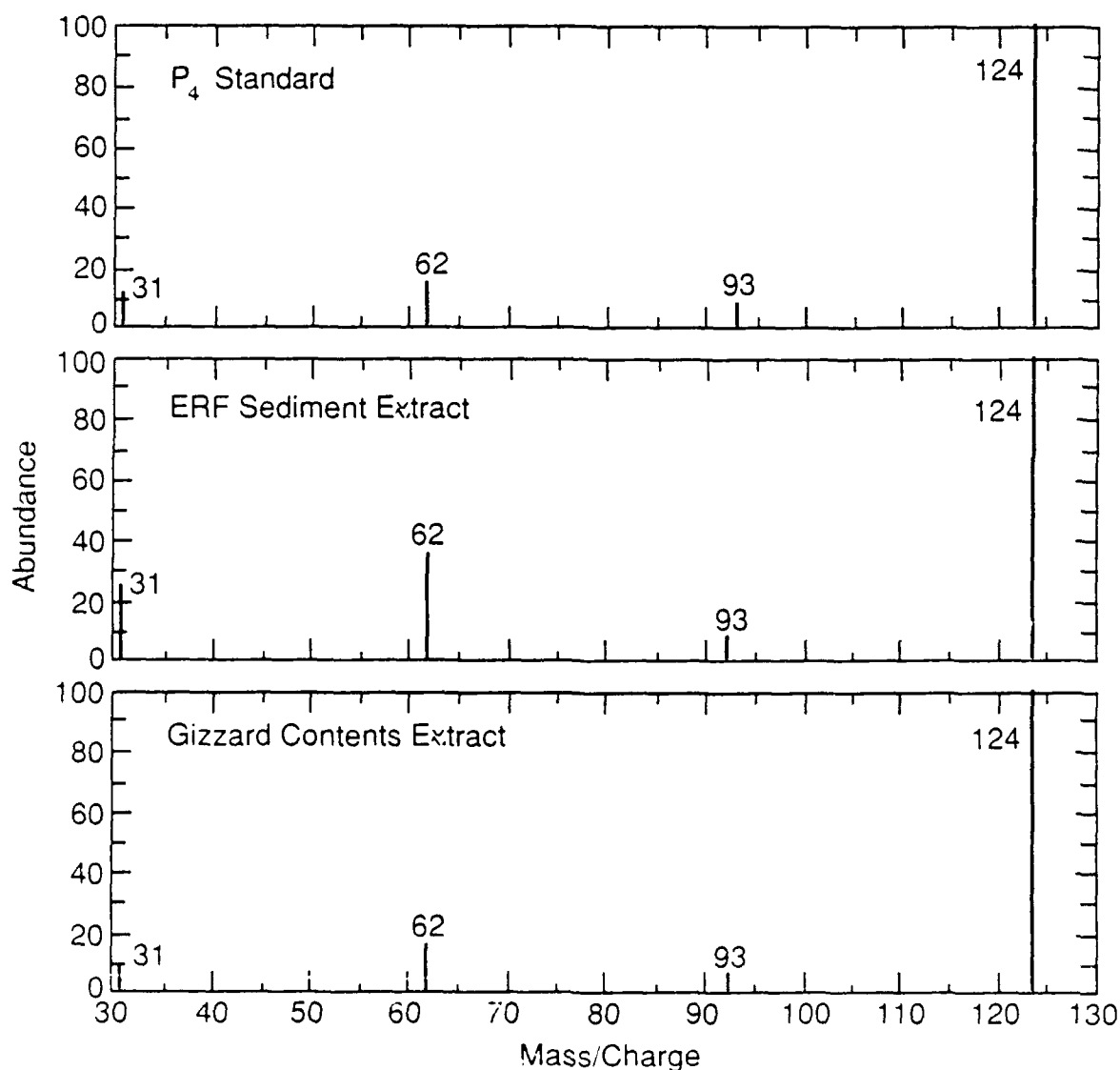


Figure 3. GCMS analysis of a sediment extract and an extract of gizzard contents.

Examination of six sediment samples revealed particulate white phosphorus in three of these samples. The white phosphorus particles were waxy, transparent yellow and very irregular in shape, with rough surfaces. The particles smoked when cut and exposed to air. Particle sizes ranged from 0.14 to 3 mm in diameter.

Observations of waterfowl behavior

During 49 hours of observations in September, we observed eight green-wing teal and one pintail duck violently convulse and subsequently die, each within four to six hours of their arrival at the pond. The first obvious signs of poisoning in each duck was rapid head-shaking and repeated drinking. This behavior alternated with periods of lethargy during which the eyes were closed. These ducks also sought shelter in tall vegetation and could be readily approached. The next symptom of poisoning was backward arching of the neck and head swaying while the bird swam in very tight circles. Finally, each duck convulsed, with its wings fully extended and its head arched backwards and tail up so that the head and tail nearly touched over the back. Most of the convulsing ducks would repeatedly somersault in the water and become entangled in vegetation. These signs of distress by poisoned ducks attracted gulls and eagles, predators that were observed to consume several dead and dying ducks.

The symptomatic behavior of mallards dosed with white phosphorus in the laboratory was similar to the behavior of wild ducks dying in Eagle River Flats. Following white phosphorus administration, normal activities were observed, including wing flapping, preening, drinking, bathing and frequent movement from the pool to the floor. Within one to two hours, violent head shakes with an open beak occurred, followed by more normal behavior with mild head shakes. Four to five hours after white phosphorus administration, each duck showed uncontrollable head-shaking with an open beak and constant drinking, followed by lethargy with the head hidden by the edge of the pool and the eyes closed. Finally, convulsions of varying magnitude occurred; these involved extension of the wings and arching of the head and neck over the back.

The behavior of the two ducks dosed with 2,4 DNT included inactivity, panting or heavy breathing with the bill open at one to two hours. Wobbling gait and shivering occurred at about four hours post-dosing. No convulsions occurred and a quiet death occurred at five to six hours. Analysis of the methemoglobin in the blood showed that within two hours after administration, the level had risen to 35% and 51% in the two ducks. The background or natural level was 6 and 14%. At all times



when blood was examined except at the zero time, the blood of the 2,4-DNT dosed ducks was chocolate-brown or the color of root beer. The presence of this methemoglobin pigment is highly diagnostic of exposure to 2,4-DNT and other nitroaromatic compounds. Blood collected from birds observed to die in ERF was always bright red, indicating that the cause of death was not ingestion of 2,4-DNT.

Analyses for white phosphorus in tissues from wild and laboratory birds

Tissues were collected from both the wild and the dosed laboratory ducks. In addition to the tissues of wild birds that were observed to die in Eagle River Flats, carcasses of several ducks and eight tundra swans found dead in Eagle River Flats were collected, frozen and shipped to the laboratory for tissue analysis. During September, five green-winged teal were trapped in Susitna Flats, another Cook Inlet salt marsh 40 km from Eagle River Flats. The tissues from these ducks were used as controls.

White phosphorus was initially confirmed by GCMS in the gizzard contents of three wild ducks (a green-winged teal, a pintail and a mallard) and one tundra swan found dead in Eagle River Flats. Subsequent analyses by GC-FPD showed that the gizzard contents of all 19 waterfowl carcasses (8 swans and 11 ducks) collected in Eagle River Flats contained white phosphorus in widely varying amounts. The mass of white phosphorus in the gizzard contents varied from a low value of 0.01 µg in a green-winged teal up to 3 mg in one mallard duck and 11 mg in a tundra swan. Clearly all of these waterfowl ingested white phosphorus. In addition, virtually all tissues including the fat, skin and livers of these birds contained detectable concentrations of white phosphorus, indicating that the compound had been absorbed from the digestive tract. Of these tissues, the fat of both wild and dosed laboratory ducks contained the highest white phosphorus concentrations, as would be expected of a lipid-soluble chemical. In contrast, none of the five green-winged teal from the Susitna Flats contained white phosphorus in either their gizzards or their body fat.

DISCUSSION

Two munitions compounds were found in ERF sediments: 2,4-DNT (a nitroaromatic compound) and white phosphorus (P₄). We concluded from the extensive sampling that high explosives are not found in the water nor in the surface sediments at ERF. The salt marsh immediately adjacent to the EOD area is contaminated, however, with propellants, as shown by the distribution of samples contain-



ing 2,4-DNT. The source of this contamination was probably the improper demolition of propellants in the EOD area. The whole grains of propellant found on the EOD pad and in the adjacent salt marsh also suggest that incomplete demolition of these propellants resulted in contamination of both the EOD pad and the adjacent salt marsh. When these grains were extracted and analyzed by GCMS, the compounds found in the grain extract were identical to those found in the soil sediment extract. The spatial variability in the concentration of 2,4-DNT within sediment samples also indicates that the contamination is particulate in nature, as opposed to a plume coming from a point source.

Although 2,4-DNT was found locally in the salt marsh up to 50 m from the edge of the EOD area, several lines of evidence suggest that 2,4-DNT is not the cause of waterfowl mortality in ERF:

- The behavior of ducks dosed with 2,4-DNT in the laboratory was not consistent with that of sick wild ducks in ERF.
- 2,4-DNT has a relatively high acute dosage (1000 mg/kg of body weight). The highest concentration of 2,4-DNT found in ERF sediment was about 60 µg/g. For a duck to consume a lethal dose, 17 kg of sediment would have to be processed.
- Methemoglobin, as indicated by blood color, was not visually obvious in any of the ducks autopsied in the field.
- The area where 2,4-DNT was found is mostly tall sedge marsh with few ponds suitable for waterfowl habitat.

All evidence indicates that white phosphorus, as a particulate in the sediments, is responsible for the death of waterfowl in Eagle River Flats:

- White phosphorus is highly toxic to waterfowl at ingestion levels of 1.5–3 mg/duck (Coburn et al. 1950).
- White phosphorus was detected by gas chromatography in the gizzard contents and fat of all 11 dabbling duck and 8 tundra swan carcasses collected in Eagle River Flats but in none of five healthy teal collected in a nearby salt marsh.
- White phosphorus was similarly detected in several sediment samples from the bottom of the pond in which ducks feed and were observed to become sick.
- Sand-sized particles of white phosphorus (0.015–1.0 mm) were isolated from some of these sediment samples as well as from the gizzard of one duck. These sand-sized particles are probably easily distinguished and selected by sediment-feeding waterbirds from the silt and clay-sized particles (0.0002–0.005 mm) that make up the salt marsh sediments.



- Dosed laboratory adult mallards showed almost identical behavioral symptoms to those of wild ducks observed to become sick and die in Eagle River Flats.

White phosphorus is a highly reactive compound that does not occur naturally, although it has been introduced to aquatic environments by wastewater discharges from arsenals (Pearson et al. 1976) and white phosphorus production facilities (Idler 1969). Eagle River Flats was contaminated by the firing of white phosphorus containing smoke projectiles. When a smoke projectile bursts, particles of white phosphorus ignite. When these burning particles hit water, they would be extinguished. Because white phosphorus has a high density and a low water solubility, particles would sink through the water column into the sediments. Once white phosphorus particles settle to the bottom of a shallow pond, periodic tidal flooding of the ponds with silt-laden waters would cover the particles. Bottom sediments in these ponds are anaerobic, providing a suitable environment for white phosphorus storage. Redox potentials measured in the ERF sediments in which white phosphorus was found were less than -200 mV. Oxidation in these anaerobic conditions will be extremely slow (Davidson et al. 1987, Sullivan et al. 1979). Thus white phosphorus in the sediments of ERF could be stored indefinitely and will continue to be a hazard to waterfowl even without additional inputs.

CONCLUSIONS

- Eagle River Flats was found to be contaminated with white phosphorus, a substance highly toxic to waterfowl and other animals.
- A localized area of a tall sedge marsh adjacent to an explosive ordnance disposal site was found to be contaminated with 2,4 DNT (a propellant ingredient). Improper disposal of excess propellant on this EOD site is the probable source of this contamination. Field, literature and laboratory studies show that it is unlikely that 2,4 DNT is the cause of waterfowl mortality in ERF.
- We have conclusive evidence that white phosphorus (P_4), fired into ERF in smoke projectiles, is the cause of waterfowl mortality in ERF.
- Even without additional inputs of white phosphorus, poisoning of waterfowl will likely continue in ERF. Water and sediment conditions in this salt marsh are conducive to long-term storage of white phosphorus in the sediments.



- The future military use of ERF needs to be evaluated in relation to the importance of the area as migratory waterfowl habitat, the fate and longevity of white phosphorus contamination, the other impacts of munition use and the importance of ERF as a training range for the 6th Infantry Division.
- Since we do not know with accuracy the distribution in the sediments (both vertical and horizontal) or the actual amounts of white phosphorus in ERF, additional sampling will be conducted to determine the extent of white phosphorus contamination in ERF.

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SELECTION AND PERFORMANCE OF A GROUND WATER EXTRACTION SYSTEM AT SACRAMENTO ARMY DEPOT WITH WATER TREATMENT USING ULTRAVIOLET RADIATION/HYDROGEN PEROXIDE OXIDATION

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Anne Marie Collins¹

ABSTRACT

Ground water beneath the Sacramento Army Depot (SAAD) is being extracted and treated as part of a ground water remediation program. The extraction system is achieving contaminant capture, and the ultraviolet radiation/hydrogen peroxide (UV/H₂O₂) unit is achieving necessary treatment at less than design power dosage.

INTRODUCTION

The SAAD was established as the Sacramento Signal Depot at its present location in April, 1945 and was redesignated as the Sacramento Army Depot in August, 1962. The SAAD is an electronics supply depot responsible for the storage, issue, maintenance and repair of assigned electronics supplies and commodities.

The SAAD occupies approximately 485 acres in Sacramento, California. The SAAD is located approximately seven miles southeast of the city's central business district. Figure 1 shows the SAAD location in relation to the center of Sacramento.

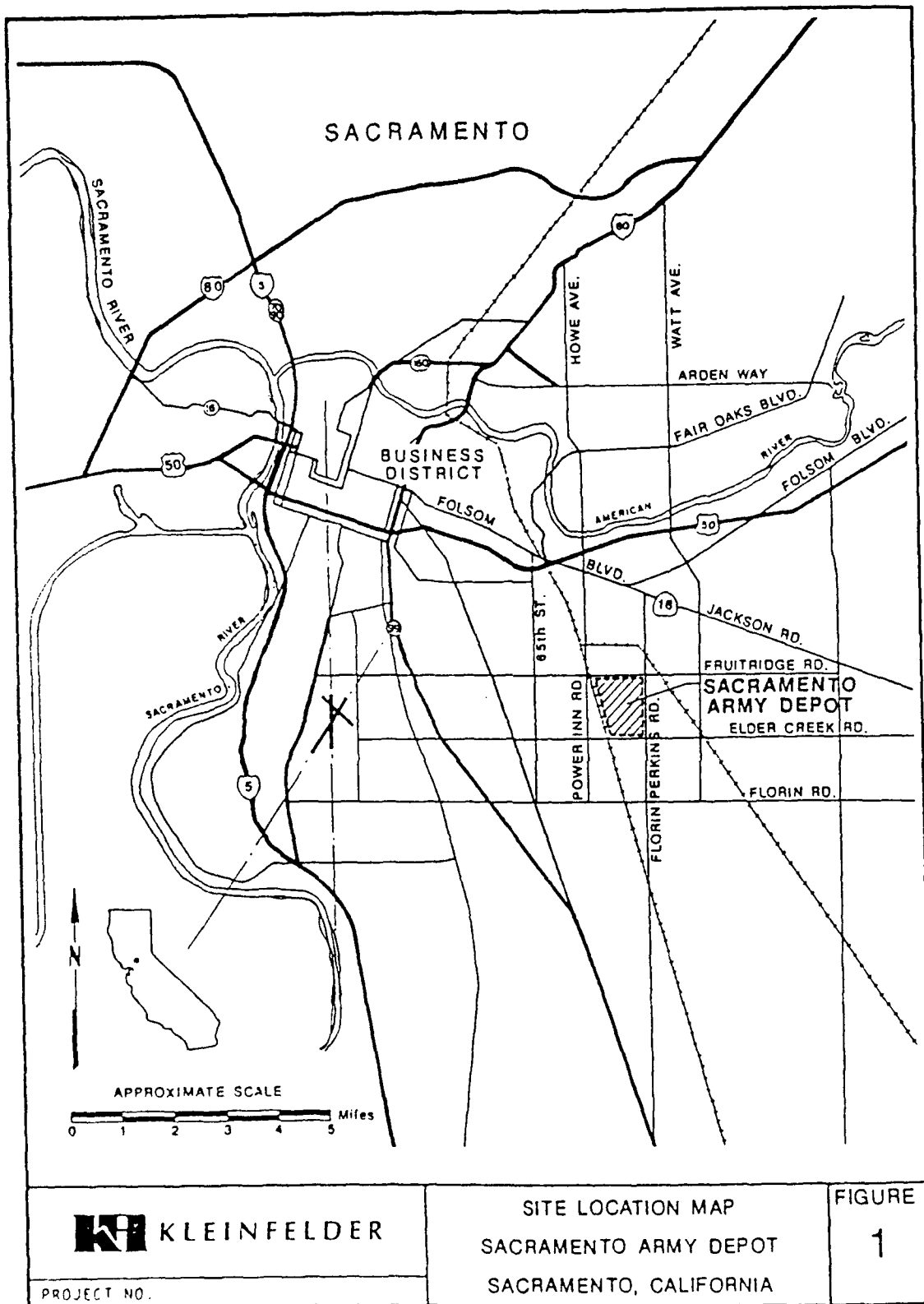
From 1965 to 1974, the SAAD was involved in various operations including night vision device repair and automatic data processing. Current depot operations include shelter repair, electro-optics, equipment repair, and metal coating and treatment. A variety of hazardous and flammable materials are reported to have been used at the SAAD including organic solvents, oils and grease, fuels, lubricants, caustic solvents and metal plating baths.

CONTAMINANTS OF CONCERN AND TREATMENT OBJECTIVES

As a result of the activities described above, and the disposal of associated waste streams, contaminants have migrated into portions of the shallow aquifers beneath the SAAD. Ground water in the southwest area of the depot is contaminated with trichloroethene, tetrachloroethene, dichloroethene, and eight other volatile chlorinated organics.

The hydrogeologic information available in the area of contamination indicates the presence of a series of highly permeable channels beneath the site, intercalated with dense silts and clays. These units have been grouped into four water-bearing zones in the upper

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200 feet: the A zone, from 89 to 107 feet; the B zone from 110 to 148 feet; the C zone from 156 to 188 feet; and the D zone from 195 to 230 feet. The primary areas of concern are the A and B zones where a number of the priority pollutant volatile organic constituents (VOCs) are present above EPA maximum contamination levels (MCLs).

The primary contaminants of concern found in the ground waters analyzed are trichlorethene, (TCE), tetrachloroethene (PCE), trans 1,2-dichloroethene (DCE), 1,2-dichloroethane (DCA), and chloroform. Ground water constituent concentrations used as a design basis for the treatment system and the treatment objectives are shown in Table 1.

TABLE 1
SAAD GROUND WATER TREATMENT
SYSTEM DESIGN CONCENTRATIONS

Contaminant	Average ug/l	Design ug/l	Treatment Objective ug/l
chloroform	4.9	7.4	100
carbon tetrachloride	0.4	0.6	5
trichloroethene	64.2	96.3	5
tetrachloroethene	10.3	15.5	4
1,1-dichloroethane	0.5	0.8	20
1,1-dichloroethene	0.3	0.5	6
1,1,1-trichloroethane	0.1	0.2	200
trans-1,2-dichloroethene	8.6	12.9	16
1,2-dichloroethane	0.9	1.4	1
methylene chloride	0.3	0.5	40
bromodichloromethane	0.2	0.3	100

The average concentration is the average for all monitoring through 1988. The design value is 50 percent higher than the average concentration and was used as an upper limit for process evaluation. The treatment objective is the lower of the MCL or California Department of Health Services (DHS) applied action level as existed at the time of the design.

Treatment objectives were applied both as a goal for ground water remediation and a quality objective for treating extracted water. Modeling indicated the need to extract ground water at up to 360 gpm (which was used in the operable unit feasibility study).

SELECTION OF THE APPROPRIATE TECHNOLOGY

The remedial action selection process consisted of identification of appropriate remedial response actions and technologies, initial screening of remedial technologies, development and screening of preliminary remedial action alternatives, and detailed analysis of the remedial alternatives. The ground water remedial alternatives considered were: air stripping with and without the use of vapor-phase activated carbon; liquid phase carbon

adsorption; and UV/H₂O₂ Oxidation. Based on the ability of UV/H₂O₂ to permanently destroy the hazardous constituents, the UV/H₂O₂ process was chosen as the remedial alternative of choice.

UV/H₂O₂ TECHNOLOGY

Unlike conventional treatment technologies such as air stripping or carbon adsorption which transfer contaminants to air or activated carbon, which, in turn, require further treatment or disposal, UV/H₂O₂ destroys the organic contaminants. The UV/H₂O₂ process uses UV light in conjunction with hydrogen peroxide (H₂O₂) to react with and oxidize organic compounds to carbon dioxide (CO₂), water, and inorganic salts.

UV/H₂O₂ destruction of organic compounds in water is a complex process involving the synergistic interaction of UV radiation and chemical oxidizers. Destruction is believed to proceed by each of the following interrelated mechanisms:

- ♦ Direct photolysis using UV
- ♦ Chemical oxidation

Direct Photolysis using UV

Adsorption of light by organic molecules increases the internal energy of the molecule. UV light at 180 to 400 nm can provide 72 to 155 kcal/mole of energy (Prengle, H.W. Jr., 1983), which is sufficient to break bond of most organic molecules. Table 2 gives the dissociation energy for several bond types.

TABLE 2
DISSOCIATION ENERGY FOR SELECTED ORGANIC MOLECULAR BONDS

Bond	Dissociation Energy, kcal/gmol
C-C	82.6
C=C	145.8
C≡C	199.6
C-F	116.0
C-Cl	81.0
C-S	65.0
C=S	166.0
C-H	98.7
-O-O-	47.0
O-O(O ₂)	119.00



As shown, UV light can provide sufficient energy to break bonds encountered in organic molecules. The rate of photolysis depends on the intensity of the UV light and the time a given molecule is exposed, i.e., the UV dosage. With enough UV dosage, organic molecules eventually are oxidized to CO₂, water, and inorganic salts. For UV, the UV dosage is related to the electrical power fed to the lamps.

Chemical Oxidation

Chemical oxidants, such as H₂O₂, destroy organic compounds by attacking bonds of the molecule and eventually cleaving these bonds to form smaller compounds. Given sufficient time, this process continues until only CO₂, H₂O, and inorganic salts remain. H₂O₂ reacts with H₂O and/or decomposes to form free radicals and atomic oxygen (Clarke, N., Knowles, G., 1982; Prengle, H.W. Jr., 1983), which account for a significant fraction of the oxidation potential of each oxidant. Hydroxyl radicals preferentially attack organic compounds by reacting with hydrogen atoms of the organic molecule, resulting in the formation of organic radicals, which can initiate other reactions (Clarke, M., Knowles, G., 1982). Free radical reactions occur rapidly; therefore, the rate limiting factor in the overall chemical oxidation mechanism is the oxidant decomposition.

A Combination of Mechanisms

In the presence of UV radiation, the rate of oxidant recombination (such as H₂O₂) is accelerated, with a corresponding increase in the rate of hydroxyl radical formation. Organic molecules that have adsorbed UV energy are in an excited state and are more susceptible to attack. Therefore, the rate at which organic compounds are oxidized is significantly higher than that attained by using UV radiation or chemical oxidants alone.

Efficiency of UV/H₂O₂

Previous studies of the UV/H₂O₂ process indicate that the overall reaction mechanism displays first-order rate kinetics with respect to the contaminant concentration, oxidant dosage, and UV intensity (Prengle, H.W. Jr, 1983). For constant oxidant dosage, the rate of oxidation can be approximated.

$$C = C_0 e^{-kt}$$

Where C = constituent concentration, ug/l
 C₀ = initial constituent concentration, ug/l
 k = rate constant for the constituent, gal/KW-min
 I = total UV intensity in reactor, KW/gal
 t = oxidation time, min

The required removal efficiency depends on the product of UV intensity and oxidation time, i.e., the oxidation of a compound at constant oxidant dosage depends on the energy delivered (UV dosage). As the UV intensity increases the oxidation time required to



achieve a desired removal decreases because the organic constituent still receives the same amount of energy. The UV dosage delivered by a particular reactor can be approximated by:

$$D = It = Pt/V$$

Where D = UV dosage, KW-min/gal
P = total UV lamp power, KW
V = reactor volume, gal.

The UV dosage is the critical parameter for UV/H₂O₂ systems. The UV dosage is adjusted by installing more or fewer lamps in the reactor. Power consumption can be optimized in the field by turning lamps on and off.

Organic carbon, soluble iron and manganese, and general turbidity can reduce the efficiency of the UV/H₂O₂ process by reducing the amount of UV energy available for adsorption by the organic contaminants and the chemical oxidant. Organic carbon will compete with the constituent of concern by adsorbing UV energy and consuming oxidant. Soluble iron and manganese will oxidize to their soluble form, thereby directly competing with the contaminant for UV energy and oxidant. Highly turbid H₂O will reduce UV intensity in a similar manner.

BENCH TESTS

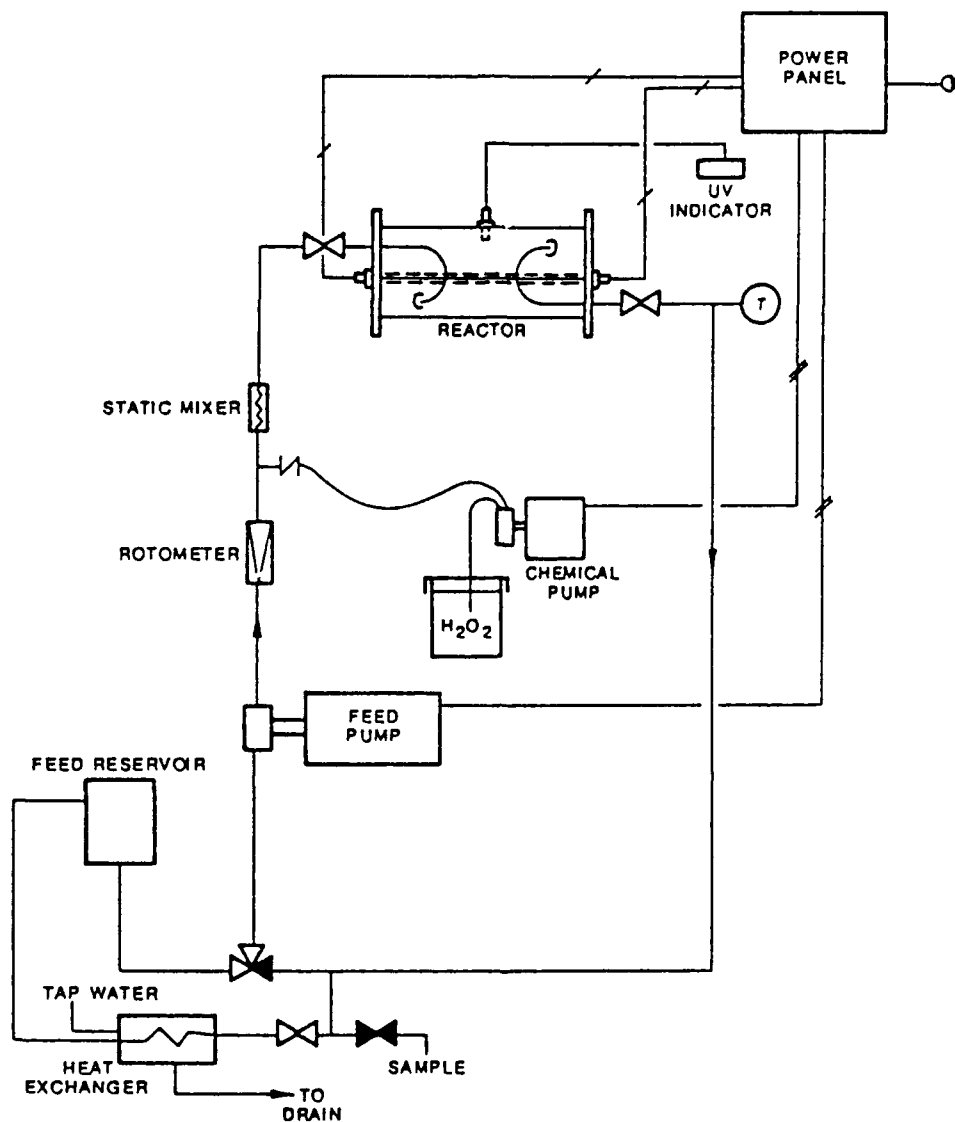
Bench scale tests of an UV/Chemical Oxidation process were performed to evaluate the effectiveness of this technology for the treatment of the SAAD ground water. Results of bench scale testing were used to assist in the design of full-scale equipment and in the development of process operating parameters such as UV dosage and H₂O₂ feed rate.

Bench tests were conducted on ground water samples collected from the SAAD site. The effect of UV and H₂O₂ dosage on removal of organic contaminants from the SAAD ground water was assessed using the apparatus shown schematically in Figure 2. A high intensity UV lamp enclosed in a quartz tube was mounted axially in a cylindrical stainless steel reactor. A variable speed pump provides process flow from a glass feed reservoir. A variable speed pulseless metering pump provides H₂O₂ injection. A heat exchanger is provided to control process temperature, as necessary. The test apparatus is closed to the atmosphere, and all wetted parts are either stainless steel, quartz, glass, or Teflon. Three tests were performed each with different UV and H₂O₂ dosages to evaluate the effect on oxidation efficiency.

EPA Method 601 results for the three UV/H₂O₂ process bench tests found that the UV/H₂O₂ process reduced all contaminants of concern to nondetectable levels before the first samples were collected. No intermediate organic compounds resulting from oxidation of the SAAD ground water contaminants were detected using Methods 624 or 625.

TCE was the anticipated rate-limiting constituent for the UV/H₂O₂ oxidation process. A TCE removal efficiency above 95 percent, which is higher than that needed for any other contaminant in the SAAD ground water, must be achieved to meet the treatment objective





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UV/H₂O₂ TEST
APPARATUS FLOW SCHEMATIC
SACRAMENTO ARMY DEPOT
SACRAMENTO, CALIFORNIA

FIGURE

2



of 5 ug/l (see Table 1). To assess the power dosage needed to achieve the SAAD treatment objectives, the rate constant for TCE oxidation was first calculated.

$$k_{TCE} = -1/It \ln (C_e/C_i)$$

Where k_{TCE} = TCE oxidation rate constant, gal/KW-min
 I = total UV intensity in the reactor, KW/gal
 t = oxidation time, min
 C_e = effluent TCE concentration, ug/l
 C_i = influent TCE concentration, ug/l

Although oxidation reaction proceeded too rapidly to allow an accurate quantification of the rate content, the minimum rate content applicable for these bench tests can be estimated by assuming the effluent concentration for the first sample collected was at the analytical detection limit for TCE of 0.12 ug/l. for the lowest H_2O_2 dosage, the calculated rate constant is 3.0 gal/KW-min. The influent concentration was 106 ug/l, the oxidation time was three minutes, and the total UV reactor intensity was 0.75 KW/gal.

The required energy dosage for the full-scale design can be calculated from the bench test data directly using the equation:

$$D = It = -1/k(C_e/C_i)$$

Where D = OV dosage, KW-min/gal

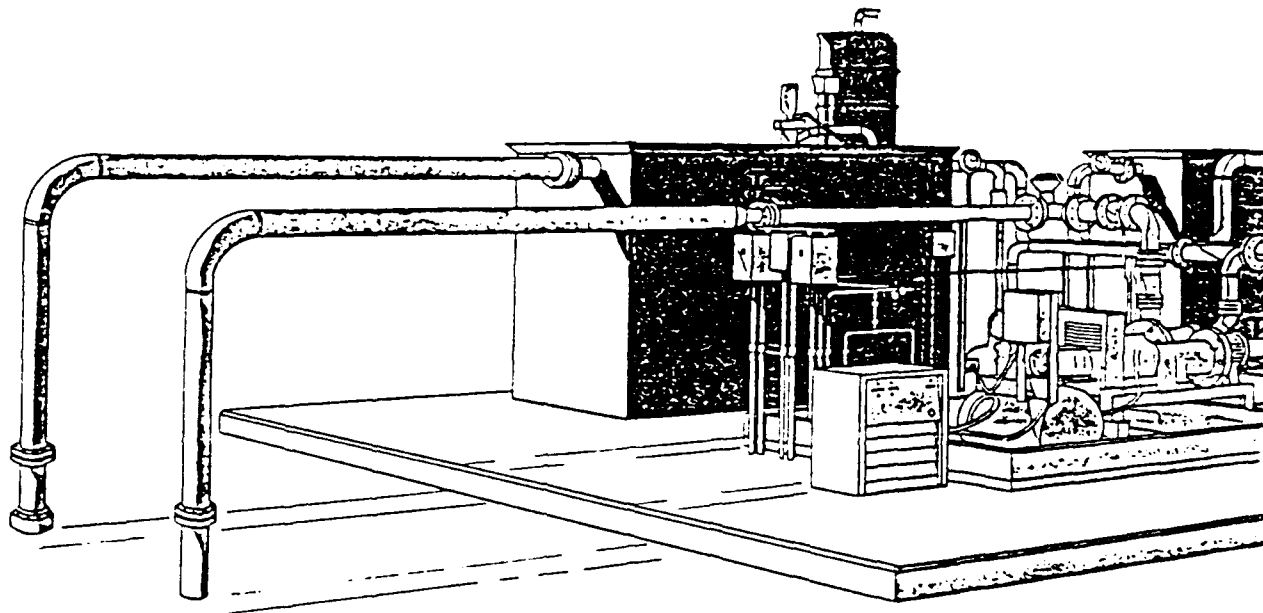
Solving the above using the calculated rate constant of 3.0 gal/KW-min, the maximum UV dosage needed to reduce the expected TCE concentration from 120 ug/l to the treatment objective of 5 ug/l is 1.0 KW-min/gal with an influent concentration of 15 mg/l. Due to inherent inefficiencies in the bench test unit, it was estimated that a full scale unit would necessarily be set a power dosage of .67 KW/gpm to achieve treatment objectives at the design conditions.

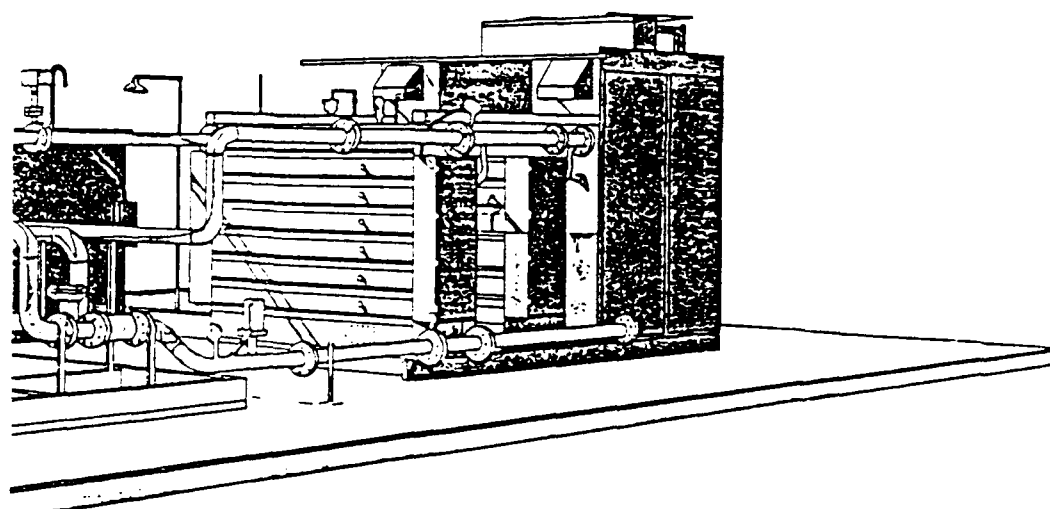
REMEDIATION SYSTEM DESCRIPTION

The extraction system consists of seven stainless steel extraction wells. Hydrogeologic information gathered during the remedial investigation indicated approximately 360 gallons-per-minute would have to be pumped from the zone A and B aquifers to intercept the ground water plume and prevent further migration.

Computer-assisted modelling of the site using MODFLOW was used to select initial area spacing. Spacing was adjusted during construction based on the field test data. The wells as installed range from 150 to 300 feet apart with varying pumping rates, depending on the production from the sand unit in which the particular well is screened.

One of the wells is located in the center of the contaminant plume, with the remaining six located along the facility boundaries in a "fence" arrangement to act as a hydraulic barrier. The wells were screened to intercept the discontinuous, high producing sand units targeted for extraction. The extraction well pumping rates range from 25 to 100 gallons-per-minute, depending on the capacity of the target extraction zones.





GROUNDWATER TREATMENT SYSTEM
SACRAMENTO ARMY DEPOT

FIGURE 3

The treatment system installed at the site is a skid-mounted, transportable, modular unit. The components include the UV reactor, lamps and power transformers, and the hydrogen peroxide feed systems. UV lamps in quartz sheaths are installed in a horizontal arrangement and evenly distributed throughout the reactor. Figure 3 is a schematic of the UV/H₂O₂ unit. The system is capable of up to 1.0 KW/gpm. Hydrogen peroxide dosage can be varied as required.

SYSTEM OPERATION

The ground water extraction and treatment system installed at the SAAD began operating in November, 1989. Early operation experienced random shutdowns. The cause of these shutdowns was unknown. Troubleshooting checks revealed that the flow meter in the UV/H₂O₂ unit was malfunctioning. It would register errant readings and then zero out during apparently normal operation, causing the treatment system to shut down. The UV interlock would open and de-energize a flow-switch which would, in turn, de-energize the Master Control Relay (MCR) and open circuits to the pumps and the solenoid valve controlling the 3-way diversion valve. The flow switch was found to be "sticky" and its replacement was also recommended. These situations apparently were the cause of the random shutdowns. In September 1990, an electrical fire occurred in the unit. Repairs were effected by the manufacturer. Other than the above, operation and maintenance of the system has been routine.

EXTRACTION SYSTEM PERFORMANCE

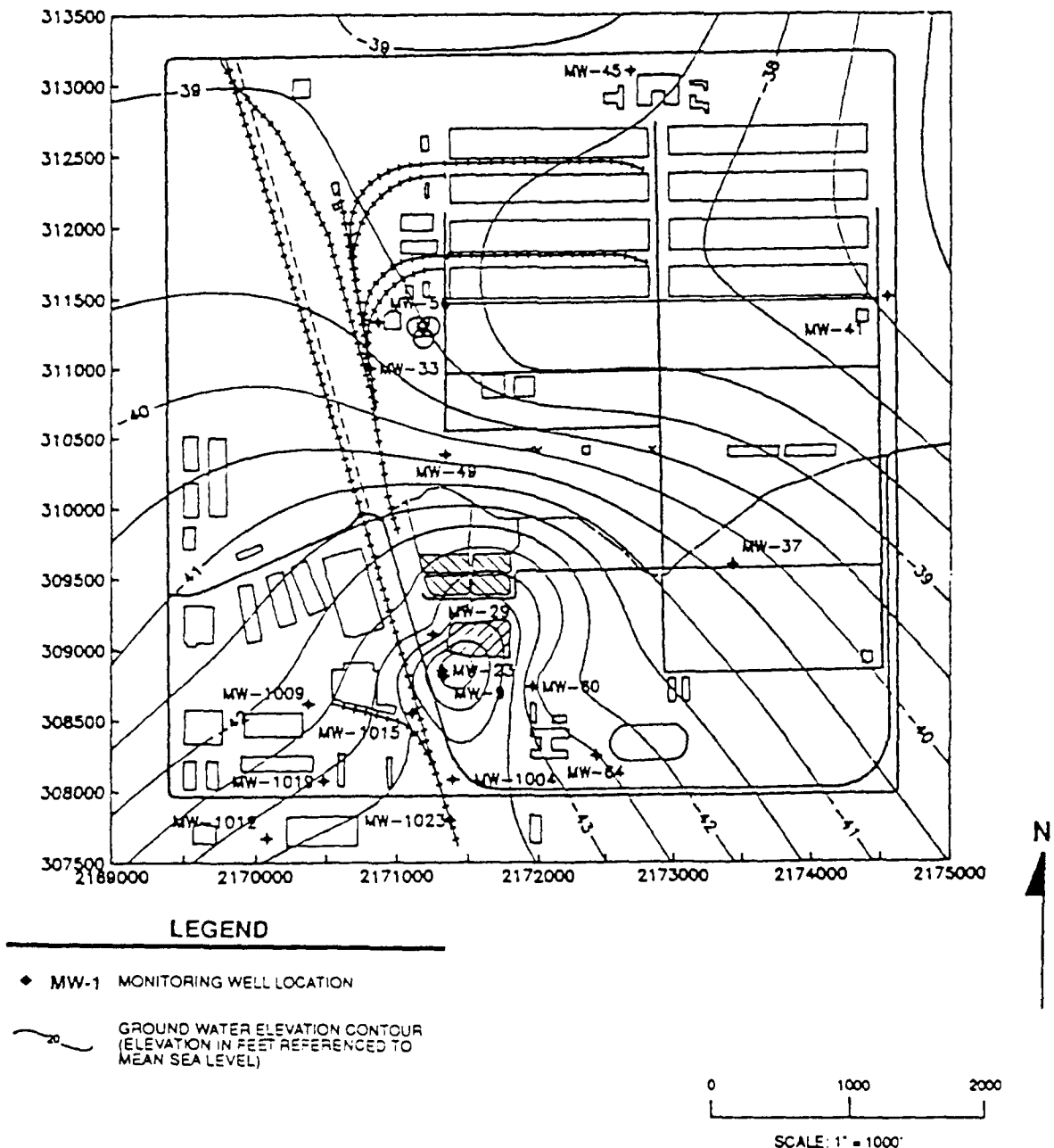
The extraction wells and treatment plant were completed in November 1989. The influent of the system was first sampled on November 30. The following TCE concentrations were detected in the treatment plant influent samples:

◆ November 30, 1989	TCE 62 ug/l
◆ December 6, 1989	TCE 55 ug/l
◆ January 4, 1990	TCE 42 ug/l
◆ February 15, 1990	TCE 49 ug/l
◆ March 1, 1990	TCE 34 ug/l
◆ May 14, 1990	TCE 28 ug/l
◆ June 18, 1990	TCE 48 ug/l
◆ October 19, 1990	TCE 21 ug/l
◆ November 16, 1990	TCE 16 ug/l
◆ December 19, 1990	TCE 0.6 ug/l
◆ January 16, 1990	TCE 18 ug/l
◆ February 19, 1991	TCE 23 ug/l

Since the treatment system started, there has been a steady decrease in the TCE concentrations detected in the influent. Since the extraction was started in November of 1989, the lateral extent of TCE contaminant has been reduced.

From December 1989 through December 1990 this pumping activity was evident within the A and B zones. The overall drop in ground water elevations in the vicinity of the extraction system has ranged from approximately 2.5 to 5.0 feet. Pumping of the extraction wells has increased the overall ground water drawdown near the southwest corner of the SAAD and has influenced the flow direction and ground water gradient southwest of the SAAD.

January 1991 Ground Water Elevations — Zone B




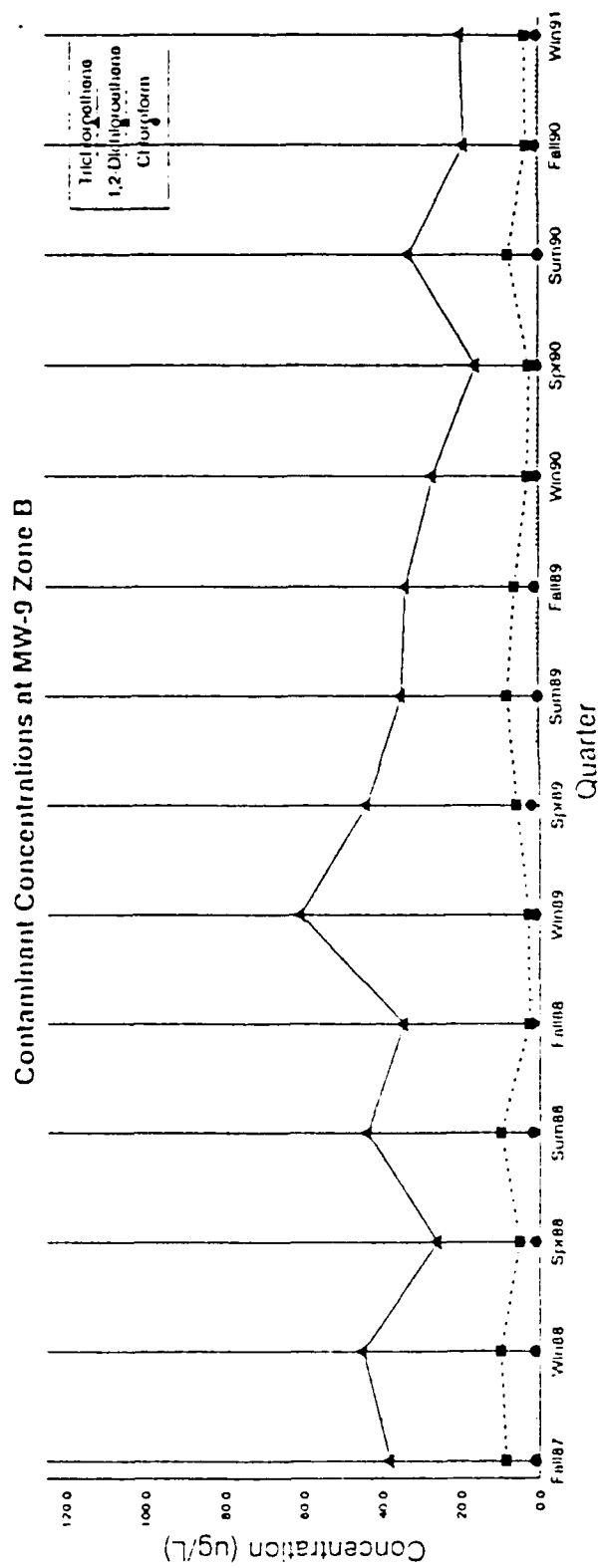
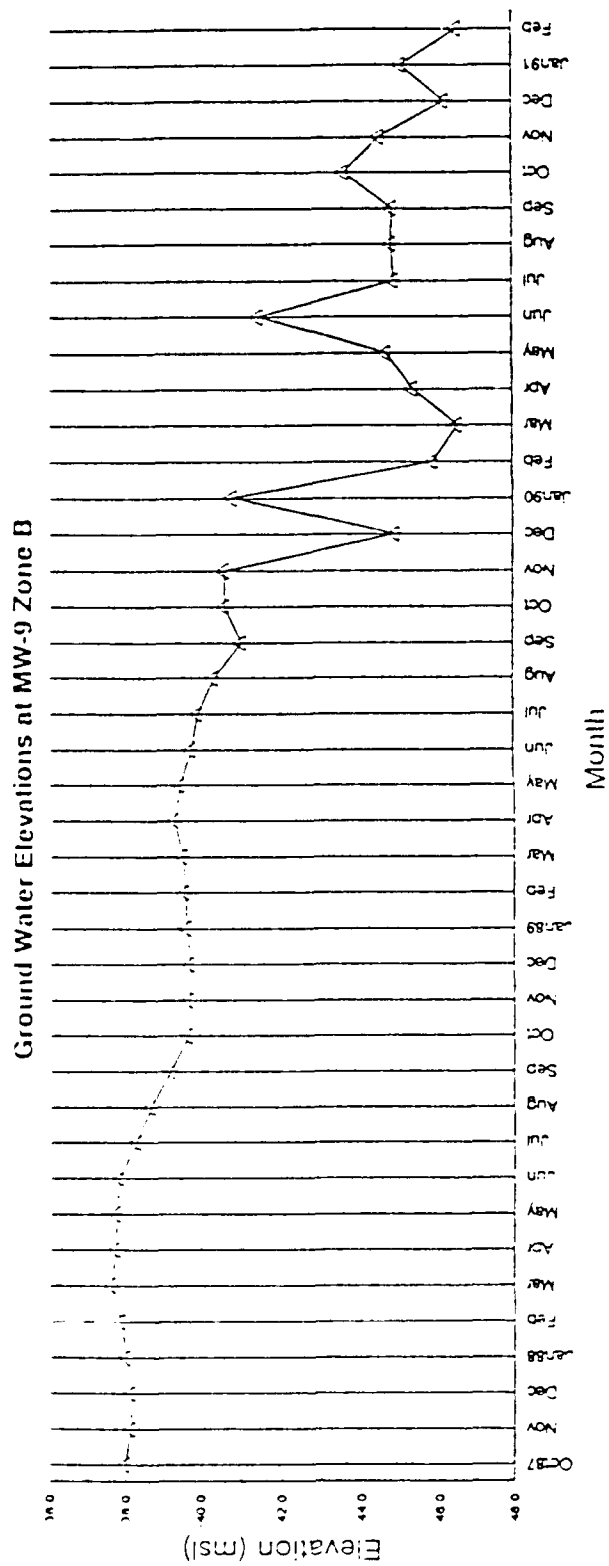
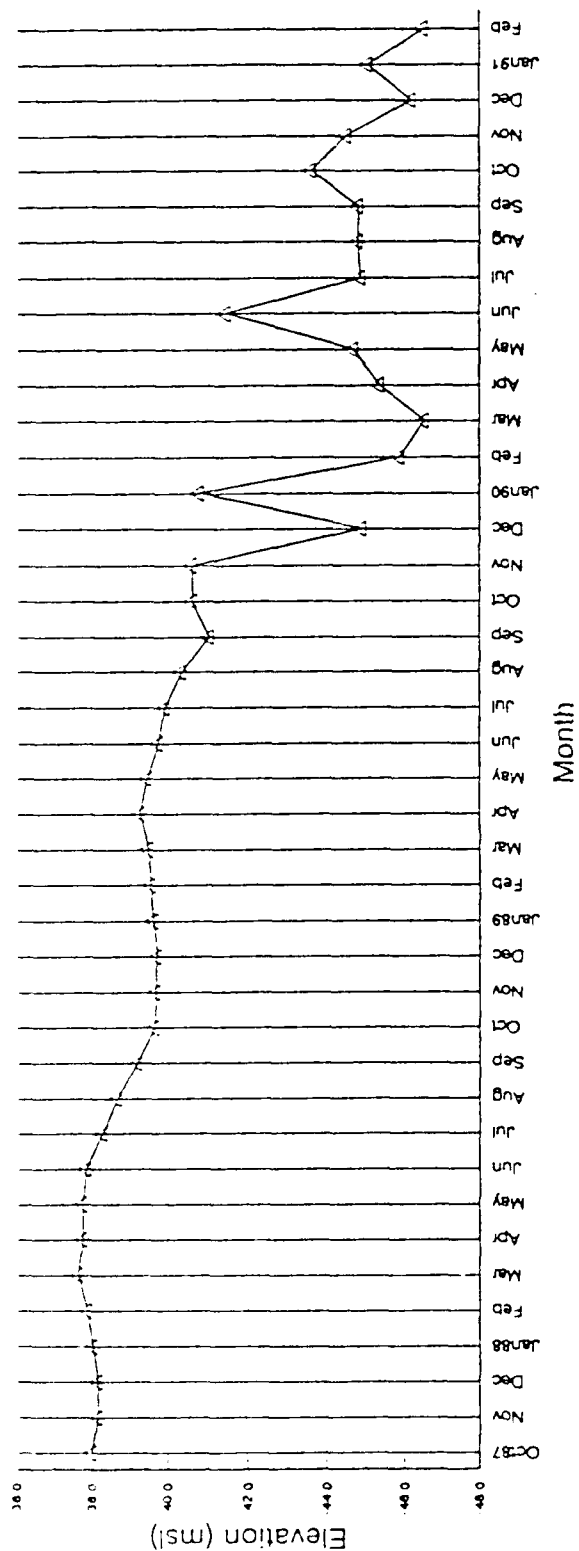
 <p>PROJECT NO</p> <p>© Kleinfelder Inc., 1991</p>	<p>GROUND WATER ELEVATION CONTOURS</p> <p>SACRAMENTO ARMY DEPOT</p> <p>SACRAMENTO, CALIFORNIA</p>	<p>FIGURE</p> <p>4</p>
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Table 3



Ground Water Elevations at MW-9 Zone B



Contaminant Concentrations at MW-9 Zone B

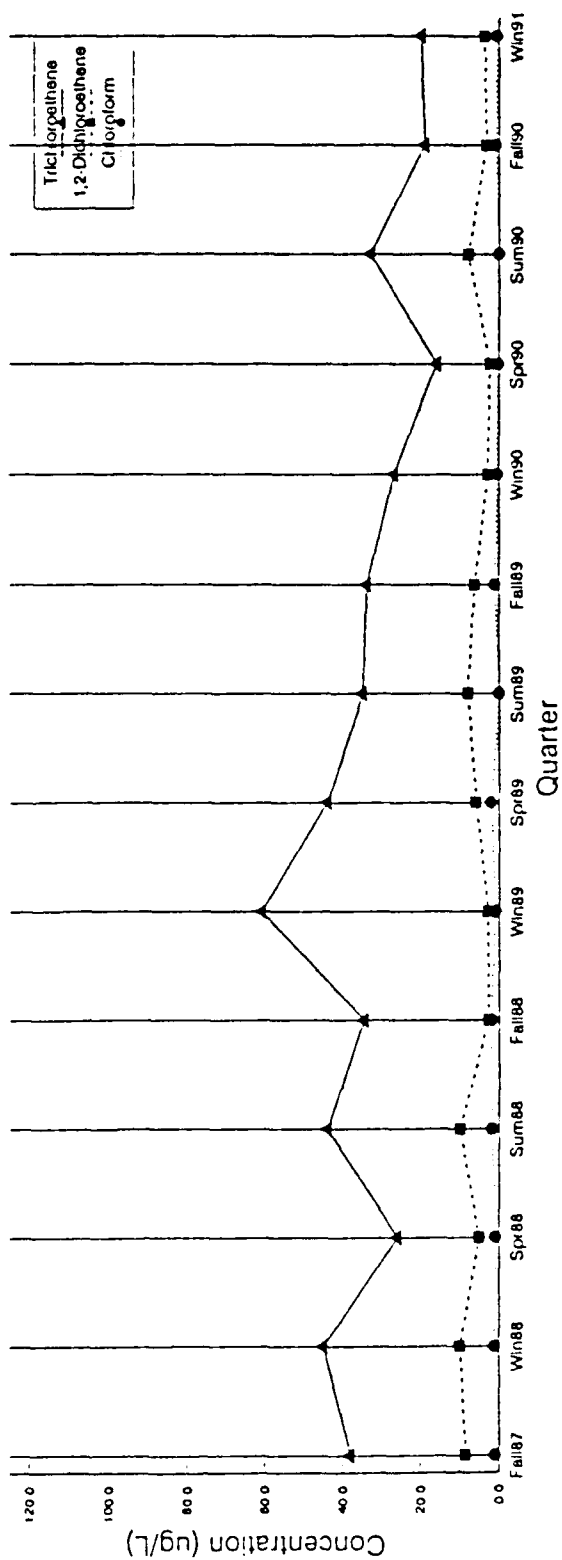


Table 4

SAAD Treatment System Operating Data

	DATA #	POWER DOSAGE	POWER KW	FLOW gpm	H2O2 % PPM	removal% TCE	removal% 1,2-DCE	removal% CHCL3	removal% 1,2-DCA	removal% PCE
H2HO < 8 ppm	10	1.0	360.0	360.0	6.0	99.6	96.2	42.1	41	77.8
	11	1.0	360.0	360.0	3.0	97.3	97.8	15.4	44.7	50
	12	1.0	360.0	360.0	1.0	81.6	80.5	20.6	3.5	81.1
	16	0.3	120.0	360.0	2.0	75.5	71.6	10	14.5	66.1
	28	0.3	120.0	370.0	0.1	86.6	90	21.4	12.8	84.6
H2O2 8-10 ppm	9	1.0	360.0	360.0	10.0	99.6	96.3	63.3		72.9
	30	0.3	120.0	370.0	10.0	93.1	95.3	33.1	29.5	84.6
	32	0.4	120.0	290.0	10.0	96.1	94.9	52.9	50	85.7
	35	0.4	120.0	270.0	10.0	96.4	94.2	53.3	39	87.5
	44	0.6	120.0	190.0	10.0	96.7		42.9		
	15	0.3	120.0	360.0	8.0	91.0	93.9	45	22.8	75.3
H2O2 11-20 ppm	3	1.0	360.0	360.0	15.0	99.6	95.4		54.5	70
	4	0.8	300.0	360.0	20.0	99.6	96.3	97.1	58.3	60.8
	13	0.3	120.0	360.0	15.0	96.2	96.3	60.9	38.8	73.7
	14	0.3	120.0	360.0	12.0	95.3	96.3	58.9	17.8	72.6
	18	0.3	120.0	350.0	18.0	95.2	95.6	68	48	66.7
	19	0.3	120.0	350.0	17.0	96.2	97.3	18.75	47.3	78.5
	37	0.5	120.0	260.0	12.0	95.8	92.5	35.7	61.5	90.5
	42	0.6	120.0	210.0	15.0	96.7	94.5			77.8
H2O2 > 21 ppm	2	0.6	180.0	320.0	25.0	99.4	97.7	45	50	55.6
	5	0.7	240.0	360.0	25.0	99.6	96.1	66.7	74.5	63.6
	6	0.5	180.0	360.0	25.0	99.1	96.8	72.2	62.1	58
	7	0.3	120.0	370.0	25.0	97.4	96.6	65.6	58.3	66.7
	8	0.2	60.0	370.0	25.0	81.7	88.4	10.5		67.2
	17	0.4	120.0	360.0	25.0	97.7	95.4	74.2	67	76.7
	20	0.5	120.0	250.0	22.0	96.6	96.2	55.3	62.1	84.6
	25	0.3	120.0	350.0	23.0	97.3	96	58.6	70	87.5
	40	0.6	120.0	200.0	25.0	97.6	96.1	31		
	22	0.5	120.0	250.0	30.0	99.5	95.8	63.9	52	89
	27	0.2	60.0	370.0	28.0	77.4	87.5	31.3	50	68.2

Table 5

A ground water elevation contour for the extraction zone in the winter of 1991 is provided as Figure 4. Historical trend charts for both of the upper water zones from our extraction area monitoring well is shown as Tables 3 and 4.

TREATMENT SYSTEM PERFORMANCE

Power dosage in the field has generally varied from 0.3 to 1.0 KW/gpm and hydrogen peroxide residuals (i.e., the measured H_2O_2 in the effluent of the reaction chamber) have varied from about 8 ppm to over 20 ppm. Design treatment efficiency for TCE has been achieved at approximately 0.35 KW/gpm as a residual hydrogen peroxide level of 8 - 10 ppm. Treatment efficiencies of TCE appear to drop off sharply at about .3 to .4 KW/gpm and at hydrogen peroxide levels below about 6 ppm.

Current actual required treatment efficiency for TCE at this site is calculated to be about 80 to 90 percent; considerably lower than the design due to the lower than design influent TCE concentrations. The unit has generally been operating with effluent TCE levels at ND (less than 0.4 ug/l) or slightly higher, rather than the 5 ug/l assumed for design. Table 5 is treatment data expressed as power dosage versus removal efficiency as a percentage. In calculating efficiency, the detection limit was used for ND. Therefore, the result may be artificially dependent on the influent concentrations. There is currently only limited data at removal efficiencies below 95 percent on which to base further conclusions regarding recommended power dosage and hydrogen peroxide residual for routine operation.

CONCLUSIONS

The SAAD is successfully remediating ground water beneath the southwest corner of the site with extraction and treatment. The treatment process employs a combination of ultraviolet radiation and hydrogen peroxide oxidation. Treatment efficiency has been higher than design at lower power dosages. The system was chosen due to its ability to destroy the contaminants completely with no "side effects".

LIMITATIONS

Only limited data has been gathered to date at this site. The operation may not be optimized. Lower power dosages may be feasible. The manufacturer of the UV/ H_2O_2 unit indicates the research and development effort are reducing power demands for newer units. On the other hand, this site has not had scaling, which has been observed at two other sites. The results should be considered site-specific and not extrapolated for other situations.



Arsenic Contaminated Groundwater Treatment Pilot Study

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ABSTRACT

Groundwater treatment for the removal of contaminants may be needed at a number of U.S. Army installations, including Army depots. Treatability testing of potentially applicable technologies may be needed to facilitate design and operation of treatment systems. The study described here is a treatability test for the removal of arsenic from groundwater. The goal of the study was to evaluate the effectiveness of ion exchange (IE), granular activated carbon (GAC), and activated alumina (AA) for the removal of arsenic from groundwater.

Laboratory IE, GAC, and AA isotherms were conducted to select the best performing carbon and resin types and the operating pH for the carbon and alumina media for further testing. Pilot scale continuous flow column tests were conducted at Sharpe Army Depot in Lathrop, California, using the two carbons (Calgon Filtrasorb 400 and Hydrodarco 3000) and the two resins (Amberlite IRA 402 and Ionac A-641) selected during the isotherm studies. Alcoa F-1 AA was also used during the pilot scale

continuous flow column tests. The carbon and AA were tested at an adjusted pH of 4.0 and the resin was tested at the natural pH of the groundwater. A pilot scale, conventional packed column air stripper was used to remove volatile organics (primarily trichloroethylene) from the groundwater prior to treatment by the pilot scale columns. The results from this investigation demonstrated that arsenic can be removed to the Safe Drinking Water Act MCL for arsenic of 50 ug/l by IE and AA systems and that AA provided significantly longer runs (as measured by bed volumes of water treated) than IE resins.

INTRODUCTION

Groundwater treatment for the removal of contaminants may be needed at a number of U.S. Army installations, including Army depots. Treatability testing of potentially applicable technologies may be needed to facilitate design and operation of remedial treatment systems. Sharpe Army Depot (SHAD), located in Lathrop, California, presently has a groundwater treatment system for the removal of trichloroethylene (TCE). The groundwater also contains arsenic, possibly of natural origin, and there may be a need to remove the arsenic prior to discharge.

The goal of this study was to examine, via pilot-scale testing, the possibility of arsenic removal from SHAD groundwater by ion exchange (IE), granular activated carbon (GAC), and activated alumina (AA) processes.

BACKGROUND



Arsenic (As) can occur in four oxidation states in water (+5, +3, 0, -3), but is generally found in the trivalent and pentavalent states. At low pH, pentavalent arsenic (As^{+5}) exists primarily as H_3AsO_4 . Between pH 3.0 and approximately pH 6.5, the predominant form is H_2AsO_4^- , while from pH 6.5 through pH 12.5, HAsO_4^{2-} predominates. Above pH 12.5, AsO_4^{3-} is the predominant species. At all pH values below approximately pH 9, trivalent arsenic (As^{+3}) exists primarily as the undissociated weak acid H_3AsO_3 . The distribution between As^{+3} and As^{+5} species is determined by the redox condition of the water, with As^{+3} being stable under reducing conditions and As^{+5} under oxidizing conditions [1]. Thus, depending upon both pH and redox potential, various arsenic species may be present. In general, arsenate is more amenable to most treatment processes than arsenite, and oxidation of As^{+3} to As^{+5} may be required.

Various treatment methods for arsenic removal have been investigated, including complexation with polyvalent metal species, coprecipitation with a metal hydroxide, coagulation, lime softening, adsorption on activated carbon, AA, and IE. As with many wastes, the optimal technologies for treatment at low contaminant levels, as often encountered in groundwater remediation, may be quite different from those conventionally employed to treat high strength industrial waste waters. Recent literature suggests that the use of AA may be the most promising treatment alternative for treatment of low levels of arsenic in groundwater. Much of the available literature on the AA treatment method involves the use of AA for the removal of arsenic from drinking water.

AA exhibits a complex surface structure and appears to remove contaminants by an ion exchange type mechanism. The pH of the feedwater, the arsenic concentration, sulfate concentration, chloride concentration, fluoride concentration and other anionic species play a major role in determining the AA capacity for arsenic removal [2]. Substantial removal of As^{+5} by AA has reportedly occurred within a pH range of 4 to 7 [3].

AA has an equilibrium capacity for As^{+5} up to 10 times greater than that for As^{+3} . This difference in capacity may be because at a pH of below 9, As^{+3} is present in a unionized form as H_3AsO_3 [4]. Oxidation of As^{+3} to As^{+5} is necessary to achieve effective arsenic removal. Chlorine has been successfully used to accomplish this oxidation [5]. Results from pilot tests on AA systems indicated that with an empty bed contact time (EBCT) of 7.5 minutes, pH adjustment to 6.0, and oxidation of As^{+3} to As^{+5} , up to approximately 16,000 bed volumes could be processed prior to reaching a maximum contaminant level (MCL) of 50 ug/l in the treated water, with a raw water As^{+5} concentration of approximately 100 $\mu\text{g/L}$ [6]. Previous laboratory studies for removal of arsenic from groundwater at SHAD indicated that continuous flow activated alumina columns could provide arsenic removal to below the MCL criterion of 50 ug/l [7].

When the adsorptive capacity of the AA is reached, it can be regenerated with a 4 to 5 percent sodium hydroxide (NaOH) solution. The general procedure for regeneration, which has been successfully used in pilot tests, includes upflow treatment followed by downflow treatment with NaOH, raw water rinse, and neutralization with

sulfuric acid. The regeneration of an AA system would generate a concentrated waste containing elevated levels of arsenic that may require disposal in an approved hazardous waste landfill. It has been reported in the literature [6] that the volume of the waste products generated during the regeneration of the AA system would be approximately 0.1 percent of the production of the system (quantity of treated water).

Limited information is available in the literature on activated carbon treatment of arsenic-contaminated water and wastewater. In one study involving arsenic removal from a potable water supply using activated carbon adsorption, 70 percent removal of As^{+5} was achieved with a raw water arsenic concentration of 200 $\mu\text{g/L}$ [8]. Another study indicated that the optimum pH for adsorption of As^{+5} on activated carbon is 4.0 [3]. A recent study in which activated carbon was used for treating a synthetic solution of arsenic indicated a GAC adsorption capacity of 2.5 lbs As^{+5} per 100 lbs of carbon [9]. Batch adsorption experiments to evaluate GAC for arsenic removal from the groundwater at SHAD indicated an ultimate capacity for arsenic at an influent concentration of 734 $\mu\text{g/l}$, 0.05 lb As^{+5} per 100 lbs carbon [7]. This is significantly lower than the GAC adsorption capacity reported in the previously mentioned study. The difference could have been due to the different sources of water with different chemical compositions used in the studies.

The IE process for arsenic removal typically involves the use of a strong-base anion exchange resin that allows the exchange of chloride ions attached to the resin with negatively charged arsenate ions (H_2AsO_4^-) in the raw water. Arsenite removal is less effective. When the adsorptive capacity of the resin is reached, the resin is regenerated

using a concentrated sodium chloride (NaCl) solution that replaces the H_2AsO_4^- with chloride ions.

The results of pilot plant testing of ion exchange treatment for removal of arsenic from drinking water at the Fallon, Nevada, Naval Air Station indicated that with a 5 minute EBCT, approximately 300 bed volumes could be processed before reaching the MCL of 50 ug/l in the treated water with a raw water arsenic concentration of approximately 100 ug/l [10]. The results further indicated that the efficiency of treatment using a strong-base anion exchange resin is dependent on the quantity of other anions in the water, particularly sulfate, which is preferentially removed before arsenic. Successful treatment of wastewater containing arsenate and arsenite with a strong-base resin, at pH values ranging from 4 to 13, is reported in the literature [8]. In an experimental study using the IE process, soluble As^{+5} at a concentration of 500 ug/l was completely removed from storm runoff water [11]. An EBCT of 3.6 minutes, hydraulic loading of 4.2 gpm/ft², and bed depth of 2 ft. were employed in the 1-in. diameter column used in the study.

One potential benefit of using a strong-base ion exchange resin over activated alumina occurs during regeneration, where sodium chloride could be used instead of caustic soda followed by an acid neutralization. The initial cost of the resin will probably be higher than AA, but the lower cost of NaCl and its easier handling may make an IE process less expensive in the long run [4]. Precipitation of alkalinity (i.e., calcium carbonate) in the IE vessel is a possible complication with an IE system [6]. This would

require the additional expense of removing the cations with a softener (cation exchanger) prior to arsenic removal.

MATERIALS AND METHODS

All tests performed during this project employed groundwater from wells at SHAD as the test water. Wells MW-403A, 407A, and 431A were used for the isotherm studies and well MW-440A was used for the pilot scale tests. Contaminant concentrations in these wells varied during the test period. Table 1 presents the analytical data obtained from initial sampling of wells MW403A, MW407A, and MW431A.

Isotherm Laboratory Tests

Isotherm tests were performed for selected IE resins, activated carbon types, and a single activated alumina at Roy F. Weston, Inc.'s (WESTON's) Environmental Technology Laboratory (ETL) in Lionville, Pennsylvania. Groundwater was collected at SHAD and shipped to ETL for testing.

Since treatment for arsenic removal at SHAD would likely be implemented following removal of TCE by air stripping in the existing groundwater treatment system, the contaminated groundwater from SHAD was pretreated for TCE removal by batch aeration using spargers. For isotherms to be conducted at other than the natural groundwater pH [12], the pH was adjusted to the desired value using sulfuric acid. Isotherm tests were then conducted on the pretreated groundwater samples.

Seven 250-ml aliquots were used for each isotherm. Tests were conducted in polyethylene bottles. Prew weighed quantities of adsorbent media were added to the groundwater aliquots to provide the required dosages. The bottles were sealed to preclude liquid and vapor losses during agitation. Samples were agitated at room temperature on a rotating laboratory shaker for a period of 24 hours. Each isotherm test included one blank, containing no adsorbent medium.

Following agitation, each sample (including the blank) was filtered through a Whatman 0.45 micron GF/F filter into a clean filter flask to remove the contaminant-laden adsorption medium. Each filtrate sample was then analyzed for total arsenic concentration.

From these data the equilibrium concentration of arsenic in the solution (C_e) and the arsenic loading on the adsorbent medium (q_e) were calculated. These data were plotted on log-log paper in accordance with the Freundlich equation for adsorption:

$$q_e = X/M = C_e^{1/n}$$

where,

- q_e = Adsorbent loading.
- X = $C_o - C_e$ the amount of arsenic adsorbed for a given volume of solution.
- M = Weight of adsorbent added.
- C_o = Initial amount of arsenic.
- C_e = Amount of arsenic remaining in solution.
- K and $1/n$ are empirical constants.

The results of these tests were used to select media to be testing in the pilot plant study phase of the project.

Pilot Plant Studies

The objective of pilot plant studies was to evaluate potential operating characteristics of selected adsorbent types under actual operating conditions, with respect to such parameters as adsorbent bed depth, hydraulic loading rate, and EBCT. Pilot scale testing of the media selected from the isotherm data was conducted at SHAD using a skid-mounted transportable activated carbon column pilot plant designed and built for USATHAMA. The system can be used to evaluate treatment using GAC, IE, or AA technologies. The plant consists of three skids and accessory tankage. One skid consists of the motor control center, feed pumps, and utility pumps. Each of the other two skids contains four plexiglas columns which hold the adsorption media to be tested. This pilot plant was designed to provide a high degree of operating flexibility, using variable bed depths and wastewater flow arrangements. Additional tanks and pumps are provided to allow for groundwater retention, pH adjustment, and flow control as necessary.

An air stripper 8 in. in diameter by 23 ft. high with 15 ft. of packing, designed for a water flow rate of 5 gpm, was used to remove TCE in the groundwater prior to treatment for arsenic.

Operation Scheme

In addition to the treatment units described above, the following additional tankage was added to the GAC/IE/AA pilot treatment system:

- Two 3,000-gal influent holding tanks to receive and hold groundwater from the selected well.

- One 2,000-gal equalization tank between the air stripper and the GAC/IE/AA unit. When required by the Project Test Plan [12], pH adjustment was carried out in this tank.
- Two 3,000-gal effluent holding tanks to retain the treated effluent to be discharged after testing, for conformance with the mandated discharge standard of 50 ug/l.

Figure 1 presents the schematic configuration of the combined air stripping/GAC/IE/AA pilot system that was used in this study. As shown in Figure 1, there were three GAC/IE/AA treatment trains. These three trains were operated in parallel to allow for study under three different experimental conditions at the same time.

In order to evaluate the need for an arsenite oxidation step during the pilot study, portions of samples from candidate wells were subjected to arsenic speciation analysis. These specialized analytical services were provided by the Benedict Estuarine Research Laboratory of the Academy of Natural Sciences.

Analytical Methods

Isotherm samples were analyzed for total arsenic at WESTON's Lionville, Pennsylvania, analytical laboratory by USATHAMA-certified Method SD01. Analysis for total arsenic during pilot studies at SHAD were conducted by WESTON's Stockton, California Laboratory using USATHAMA-certified Method SD27.

Arsenic speciation analysis was conducted by the Benedict Estuarine Research Laboratory of the Academy of Natural Sciences, using cryogenic trapping distillation and quartz furnace atomic adsorption or by a continuous flow hydride generation method (13,14).



Samples were analyzed for TCE at WESTON's Lionville, Pennsylvania, and Stockton, California, laboratories by USATHAMA Method UM14 and EPA Method 8010, respectively.

Analyses for inorganic constituents in groundwater were performed by WESTON's Lionville Laboratory using methods derived from EPA's Methods for Chemical Analysis of Water and Wastes (15) or Standard methods for the Examination of Water and Wastewater (16). Groundwater pH was measured by direct reading pH meters.

EXPERIMENTAL RESULTS AND DISCUSSION

Isotherm Testing

A single round of isotherm testing was conducted for the purpose of examining equilibrium adsorption characteristics of the various adsorption media and to select media for use in pilot testing. Preliminary selection of media types for isotherm testing was based upon literature and vendor information. Table 2 summarizes the results of isotherm testing in terms of the media selected for pilot scale evaluation. The isotherm tests performed during this study indicated that each of the major media types (IE resin, GAC, and AA) may be capable of treating arsenic-bearing groundwater at SHAD to less than 50 ug/l. The lowest required dosages (weight of adsorbent per volume of contaminated water) and highest q_e values for equilibrium adsorption were observed with Alcoa Type F1 AA. In general, the selected IE resins appeared to perform better than activated carbon when compared on the basis of adsorbent dosages, with GAC

achieving equilibrium arsenic concentrations less than 50 ug/l only at high carbon dosages.

Arsenic Speciation

Arsenic speciation in the potential pilot study supply wells was evaluated in order to determine the need for an oxidation step during the pilot study. If the groundwater at SHAD contained predominantly As^{+3} , a pre-oxidation step using chlorine as the oxidant was planned.

Sampling for the initial characterization of arsenic speciation in MW403A, 407A, and 431A took place on 28 February 1990. Additional sampling, from MW440A and at the actual pilot plant influent, took place on 23 May 1990, during the pilot plant phase of the study. Arsenic speciation data from these samples are presented in Table 3. These data demonstrate that arsenic in the sampled wells existed almost entirely ($\geq 99.5\%$) as the oxidized As^{+5} form.

The finding that the arsenic to be treated existed in the oxidized form obviated the need for a chlorine oxidation step in the pilot study. Since As^{+3} concentrations were all well below the MCL of 50 $\mu\text{g/L}$, effective removal of the pre-existing As^{+5} would likely permit attainment of the discharge standard. The incremental increase in bed life (before breakthrough at 50 $\mu\text{g/L}$ total arsenic) that might be achieved by oxidation of the low levels of As^{+3} would likely be slight.

Therefore, based upon the results of the initial arsenic speciation analysis, as confirmed in subsequent resampling during the pilot study phase, chlorine oxidation of the influent groundwater was not employed in this study.

Pilot Scale Testing

The overall objective of the pilot scale test program was to evaluate the potential performance of the selected media under continuous flow conditions simulating those likely to be employed in full scale treatment system. Specific objectives pertinent to this effort included:

- To determine the effectiveness of the media in removing arsenic to the MCL (50 ug/l) under continuous flow conditions.
- To determine the adsorption capacities of the media.
- To select the best performing media.
- To evaluate potential operating conditions for a full scale treatment system, including hydraulic loading rate and EBCT.

These objectives were addressed in a test program conducted at SHAD using USATHAMA's skid-mounted transportable pilot system described earlier. The overall duration of the pilot test program (not including mobilization and demobilization) was approximately 17 weeks. The test program encompassed a total of seven experimental runs. Table 4 presents a summary of the test program.

Each adsorbent bed rested upon a 1-ft-thick base consisting of a layer of stone sandwiched between two layers of borosilicate glass wool, specified as being free from heavy metals, fluorine, and alumina. Adsorption media were prepared as water slurries.

allowed to soak overnight, and then added to the columns to provide a settled bed depth of 4 ft. The column was sealed, leak tested, and backwashed prior to commencing each test run. Once begun, each test ran continuously until breakthrough with the exception of brief shutdowns for necessary repairs. Breakthrough was defined as the Safe Drinking Water Act MCL of 50 $\mu\text{g/L}$.

Each column was backwashed as needed during the run to remove accumulated solids at the head of the column which interfered with flow and contributed to excessive head loss across the column. In general, columns were backwashed when the head loss across the column exceeded 5 psi, as indicated by the pressure gauges mounted on the inlet and outlet of each column. During backwashing, the adsorbent bed was also generally broken up, minimizing plugging or channelling of flow through the bed. In general, the duration of the backwashing operation was approximately 15 minutes.

This study evaluated the potential treatment of arsenic-contaminated groundwater by three different technologies: IE, GAC, adsorption, and AA. While the specific mechanism of arsenic removal may vary, the implementation of each of these technologies is similar, each likely employing a series of fixed bed down flow treatment columns (although other configurations are possible) with varying degrees of pretreatment and/or post treatment. Therefore, the performance of the different media can be compared in part on the basis of the quantity of contaminated water, normally expressed in terms of bed volumes, which can be treated prior to breakthrough.

Table 5 summarizes the results of pilot tests conducted in this study in terms of the quantity (bed volumes) of contaminated groundwater treated under various operating



conditions prior to breakthrough in the primary column effluent, with breakthrough being defined as effluent arsenic concentrations equal to or exceeding the Safe Drinking Water Act MCL of 50 $\mu\text{g/L}$.

These data indicate that both IE resins and AA can provide treatment of SHAD groundwater to levels below the MCL. The longest bed lives were achieved with AA at reduced pH, relatively low hydraulic loading rates, and contact times on the order of 9.8 to 14.7 min. Bed lives on the order of 3,000 or more bed volumes of water treated appear to be achievable in a single activated alumina column operating under these conditions. Figures 2, 3 and 4 are plots of the arsenic breakthrough curve for AA runs at various loadings. By contrast, ion exchange bed lives on the order of 200 to 500 bed volumes of water might be obtained, as shown in Table 5.

Granular activated carbon does not appear capable of meeting the arsenic treatment requirements under the conditions used in this study. In each GAC run conducted in this study, essentially immediate breakthrough of arsenic, at levels comparable to those in the influent were observed.

While it is most likely that arsenic removal from SHAD groundwater would occur after air stripping for TCE in the existing groundwater treatment system, an alternative scenario suggested arsenic removal at individual wellheads without TCE pretreatment. Consequently, several supplementary runs were conducted to evaluate the effect of TCE on removal of arsenic by AA. For these tests, groundwater from well MW44OA was spiked with TCE to a concentration of 25 $\mu\text{g/l}$. These supplementary runs were also conducted at the natural pH of the groundwater. As shown in Table 5, arsenic removal

without prior pH adjustment (Run 7c) resulted in lower bed lives than with a pH reduction step at comparable loadings (Run 5b). The presence of TCE further reduced bed lives, as shown in Runs 7a and 7b.

Definite selection between IE and AA, the two treatment technologies exhibiting satisfactory performance in this study, would depend upon analysis of the relative treatments costs, and the operating advantages/disadvantages associated with each technology. This comparative analysis would consider the capital equipment requirements as dictated by such factors as hydraulic loading and contact time, pre- and post-treatment requirements, regeneration requirements and the attrition rate and replacement costs of the media themselves. For example, although AA exhibited the longest bed lives in this study, the data indicate that a pH adjustment step is required and that relatively low hydraulic loading rates and long contact times (corresponding to relatively large adsorption units) are required. By contrast, IE data suggest relatively little dependence on loading rate and contact time over the ranges evaluated, such that relatively smaller adsorbers operating at higher loadings may prove suitable.

Regeneration of media was not addressed in this study. Since the adsorption capacities of regenerated media may differ in some respects from these of virgin media, this aspect should be addressed prior to design of a treatment system. Based upon previous research and manufacturer's recommendations (summarized in Table 6) regeneration of either IE resins or AA is a relatively straightforward operation, requiring conventional reagents, and attrition of the media during regeneration can be controlled.

With respect to media attrition and replacement, it should be noted that the IE resins recommended by vendors for use in this study were relatively expensive as compared to, for example, conventional softening resins. The recommended resins cost approximately \$230/ft³. By contrast, the cost for the AA is relatively low, at approximately \$71/ft³ (\$1.65/lb).

The following conclusions are drawn from the data obtained in this study:

- Strong base anion exchange resins (specifically Rohm and Haas IRA 402 and Sybron Ionac A-641) and AA (specifically Alcoa Type F-1, 24-48 mesh) are capable of treating arsenic-contaminated groundwater from well MW-440A at SHAD to effluent concentrations below the Safe Drinking Water Act MCL of 50 µg/L (as total arsenic). The granular activated carbons tested were not capable of effective arsenic treatment under the conditions evaluated in this study.
- Of the successful media, AA provided the longest bed lives (in terms of bed volumes of water treated prior to breakthrough at the MCL level).
- The use of AA requires a pH reduction step. Hydraulic loading rates of 2 to 3 gpm/ft² and EBCTs of 9.8 to 14.7 minutes provided the longest bed lives.
- IE resins exhibited less dependence on hydraulic loading rate or EBCT than did activated alumina. However, bed life at all loading rates was lower than with AA.
- Analytical data from wells MW-403A, MW-407A, MW-431A, and MW-440A indicate that pentavalent arsenic (As⁺⁵) is the predominant arsenic species present in SHAD groundwater and that trivalent arsenic (As⁺³) is present only in small amounts. In fact, removal of As⁺⁵ alone would be sufficient to achieve the SDWA MCL for total arsenic of 50 µg/l. As a result no oxidative pretreatment step was required or employed in this study and, as long as this situation prevails, oxidative pretreatment should not be required in a full-scale system.

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Table 1

SHAD Pilot Study Groundwater Characteristics
(22 December 1989)

Parameter	Well 403A	Well 407A	Well 431A
<u>Volatile Organics</u>			
Trichloroethene, µg/l	5 u	34	5 u
<u>Metals</u>			
Arsenic, total, µg/l	143	214	11.7
Cadmium, total, µg/l	10.0 u	10.0 u	10.0 u
Cobalt, total, µg/l	50.0 u	50.0 u	50.0 u
Chromium, total, µg/l	18.0	10.0 u	10.0
Copper, total, µg/l ^a	8.1	6.8	15.1
Iron, total, µg/l	7,070	4,020	18,000
Lead, total, µg/l ^a	9.6	16.8	15.9
Selenium, total, µg/l	6.3	9.5	5.0 u
Zinc, total, µg/l	172	71.2	196
<u>Inorganics</u>			
Ammonia nitrogen, mg/l	0.10 u	0.10 u	0.10 u
Nitrate/nitrite as nitrogen, mg/l ^b	17.7	23.5	43.1
Sulfate, mg/l	125 u	125 u	125 u
Phosphate as phosphorous, mg/l ^c	1.6	2.3	0.67 u
<u>Other Parameters</u>			
Temperature, °F	53.5	56.0	56
Conductivity, µmhos	1,479	1,250	756
pH	7.47	8.26	7.90

^aLaboratory control standards for copper and lead were outside the control limits of 80-120%.

^bMeasured as nitrite nitrogen after reduction of nitrate; MCAWW Method 353.1.

^cSamples analyzed beyond regulated holding time.

Note: u = Compound was analyzed but not detected. The associated numerical value is the sample detection limit.

Table 2

Summary of Media Selection

Adsorbent	Adsorbents Screened in Isotherms	Adsorbents Selected for Pilot Testing
Ion Exchange Resin	Rohm and Haas Amberlite IRA-402	Rohm and Haas Amberlite IRA-402
	Rohm and Haas Amberlite IRA-900	Sybron Ionac A-641
	Sybron Ionac A-641	
	Sybron Ionac ASB-1	
Activated Carbon	Calgon Filtrasorb 200	Calgon Filtrasorb 400
	Calgon Filtrasorb 300	Hydrodarco 3000
	Calgon Filtrasorb 400	
	Hydrodarco 3000	
	Hydrodarco 4000	
Activated Alumina	Alcoa Type F-1, 28-48 Mesh	Alcoa Type F-1, 28-48 Mesh

Table 3

SRAD Pilot Study
Groundwater Arsenic Speciation Data

Parameter	MW 403A 28 February 1990	MW 407A 28 February 1990	MW 431A 28 February 1990	MW 440A 23 May 1990	Pilot Plant Influent 23 May 1990
Arsenite, (As ³⁺), µg/L	0.64	0.77	0.03	0.91	0.84
Arsenate, (As ⁵⁺), µg/L	133	240	7.47	224	193
Total Arsenic (Std. Dev.), µg/L	133 (± 4.6)	241 (± 25.1)	7.50 (± 0.34)	225	194

Table 4

Summary of Pilot Study Test Runs

Test	Adsorbent (primary column)	Train	Flow rate (gpm)	Hydraulic loading (gpm/ft ²)	Bed Depth (ft)	EBCT ^a (min)	Influent pH	Dates (all 1990)	Notes
1a	IRA 402	a	0.2	2	4	14.7	natural ^b	19-26 March	
1b	IRA 402	b	0.3	3	4	9.8	natural	19-24 March	
1c	IRA 402	c	0.7	7	4	4.2	natural	19-23 March	
2a	A-641	a	0.2	2	4	14.7	natural	29 March - 3 April	
2b	A-641	b	0.3	3	4	9.8	natural	29 March - 2 April	
2c	A-641	c	0.7	7	4	4.2	natural	29 March - 1 April	
3a	Hydrodarco 3000	a	0.7	7	4	4.2	14	28 April - 29 April	
3b	Hydrodarco 3000	b	0.2	2	4	14.7	14	28 April - 29 April	
3c	Hydrodarco 3000	c	0.3	3	4	9.8	14	28 April - 29 April	
4a	Filtrisorb 400	a	0.3	3	4	9.8	14	1 May	
4b	Filtrisorb 400	b	0.7	7	4	4.2	14	1 May	
4c	Filtrisorb 400	c	0.2	2	4	14.7	14	1 May	
5a	Alcoa F-1	a	0.2	2	4	14.7	4-6	5 May - 17 June	
5b	Alcoa F-1	b	0.3	3	4	9.8	4-6	5 May - 30 May	
5c	Alcoa F-1	c	0.7	7	4	4.2	4-6	5 May - 13 May	
6a	Filtrisorb 400	c	0.2	2	4	14.7	natural	9 June	distilled H ₂ O slurry
6b	Filtrisorb 400	c	0.1	1	4	29.	natural	10 June - 11 June	distilled H ₂ O slurry
7a	Alcoa F1	a	0.2	2	4	14.7	natural	21 June - 28 June	with TCE spike
7c	Alcoa F1	c	0.3	3	4	9.8	natural	21 June - 27 June	with TCE spike
7c	Alcoa F1	a	0.3	3	4	9.8	natural	3 July - 13 July	with no TCE spike

^aEBCT = Empty bed contact time.^bpH of influent generally ranged between pH 8 and pH 9.

Table 5

Summary of Pilot Test Results

Test	Medium	Hydraulic Loading Rate (gpm/ft ²)	EBCT (min)	Influent ^a Arsenic (µg/L)	Influent pH ^c	Bed Volumes of Water ^b Treated (Approximate)
1a	IRA402	2	14.7	227.8	Natural ^c	450
1b	IRA402	3	9.8	227.1	Natural	375
1c	IRA402	7	4.2	200.5	Natural	510
2a	A-64.1	2	14.7	238.7	Natural	285
2b	A-64.1	3	9.8	252.8	Natural	250
2c	A-64.1	7	4.2	225	Natural	210
3a	Hydrosorb 3000	7	4.2	--	14	--
3b	Hydrosorb 3000	2	14.7	--	14	--
3c	Hydrosorb 3000	3	9.8	--	14	--
4a	Filtrisorb 400	3	9.8	--	14	--
4b	Filtrisorb 400	7	4.2	--	14	--
4c	Filtrisorb 400	2	14.7	--	14	--
5a	Alcoa F-1	2	14.7	196.1	4-6	3,700
5b	Alcoa F-1	3	9.8	212.7	4-6	3,475
5c	Alcoa F-1	7	4.2	257.8	4-6	2,100
6a	Filtrisorb 400	2	14.7	--	Natural	--
6b	Filtrisorb 400	1	29.4	--	Natural	--
7a	Alcoa F-1	2	14.7	181.6	Natural	500
7b	Alcoa F-1	3	9.8	179.9	Natural	525
7c	Alcoa F-1	3	9.8	202.9	Natural	850

^aWeighted average concentration.^bVolumes treated prior to breakthrough effluent arsenic concentration ≥ 50 µg/L.^cpH of influent generally ranged between pH 8 and pH 9.

Table 6

Regeneration Requirements

Ion Exchange

Example: IRA-402:

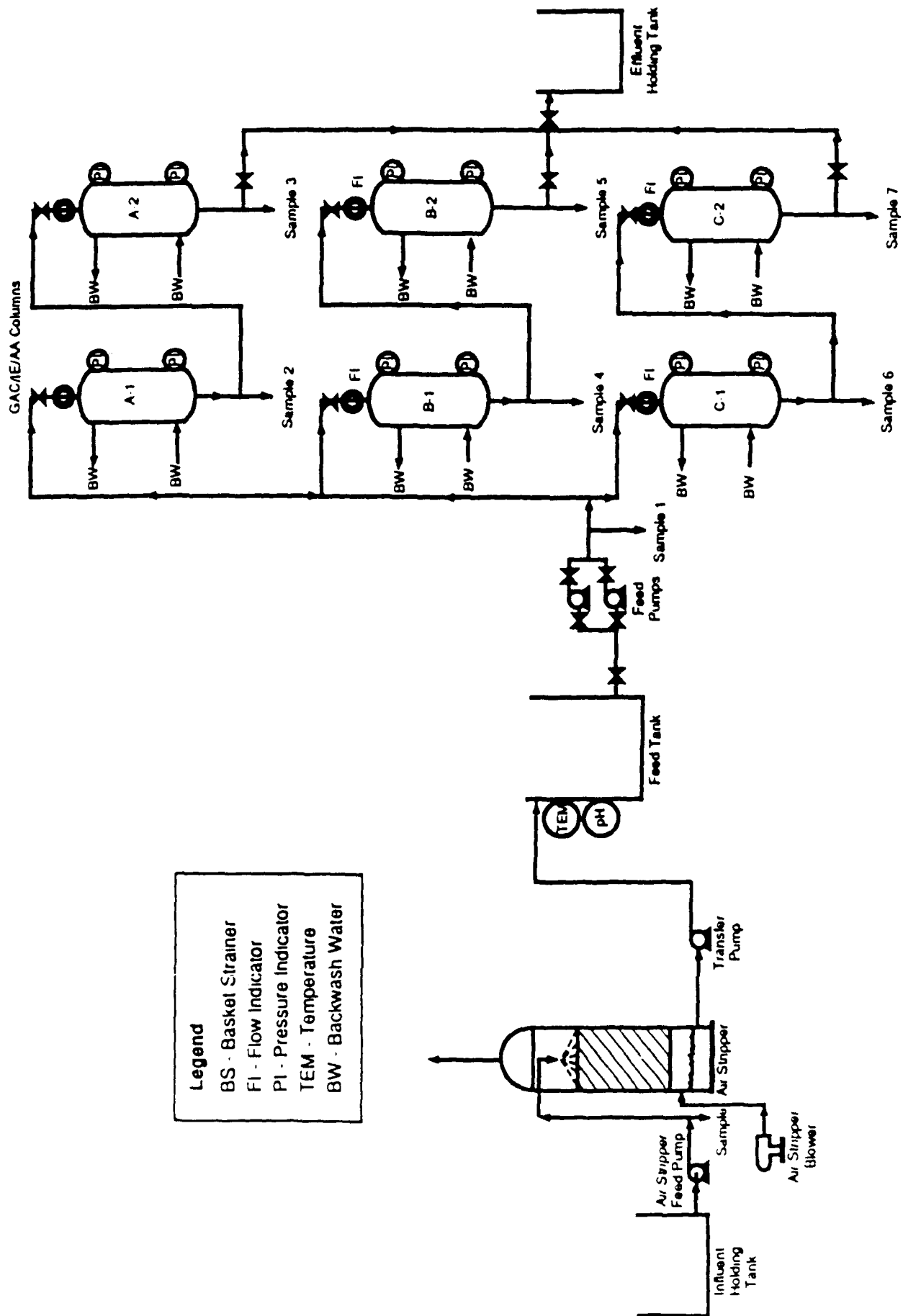
1. NaCl, 5-10% solution, ± 4 lb. salt/ft³ resin, at 0.25
1.0 gpm/ft³
2. Rinse with water.

Source: Amberlite IRA-402 Technical Literature

Activated Alumina

1. Regeneration, NaOH, 1% solution, 4 bed volumes.
2. Rinse with water, 8 bed volumes minimum.
3. Acid rinse, 0.05 N H₂SO₄, 1 bed volume minimum.
4. Final rinse, water, 1 bed volume.

Source: References 11, 12, and 17



Legend
 BS - Basket Strainer
 FI - Flow Indicator
 PI - Pressure Indicator
 TEM - Temperature
 BW - Backwash Water

FIGURE 1 Pilot treatment unit configuration.

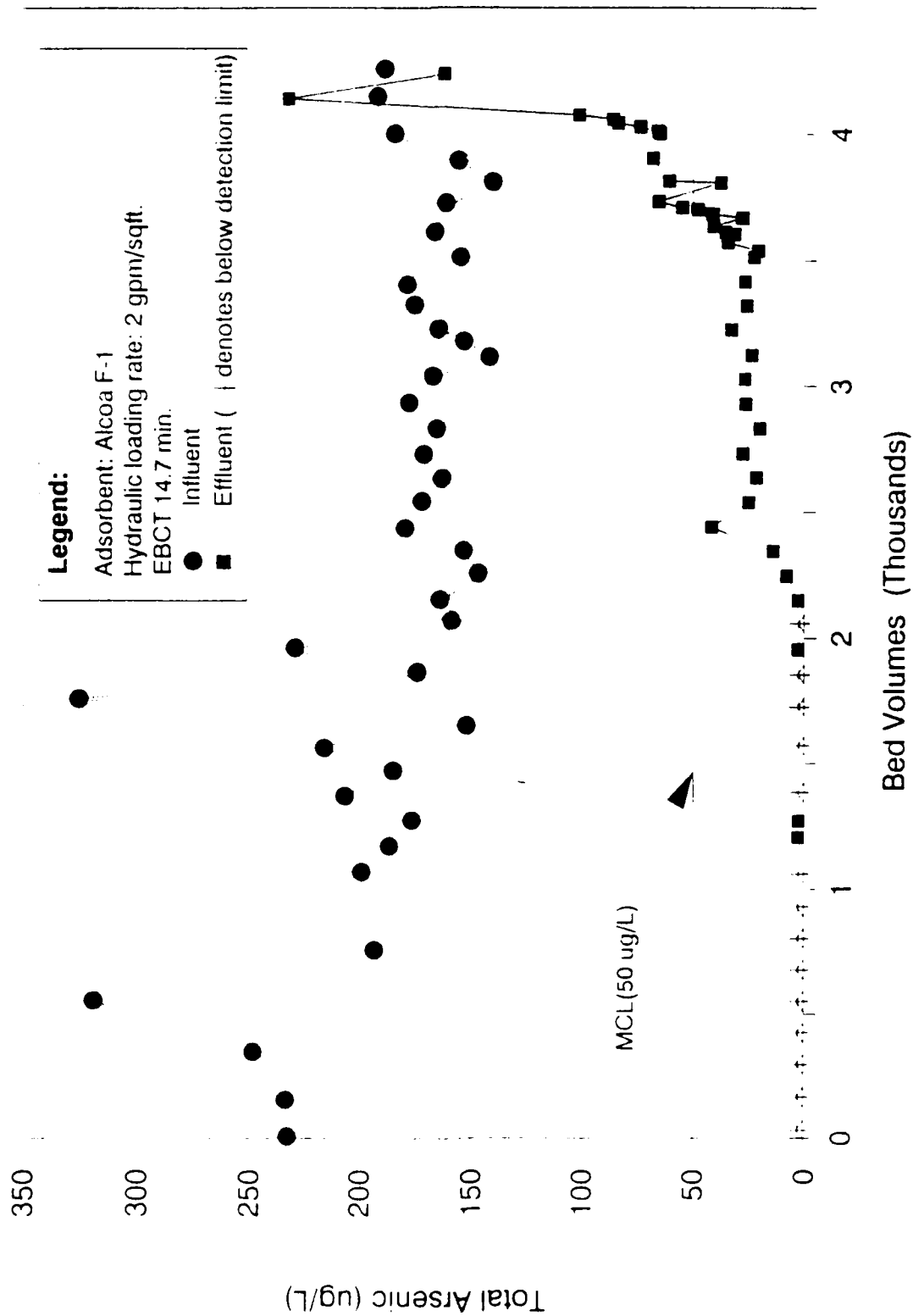


Figure 2. Arsenic removal results, Run 5a.

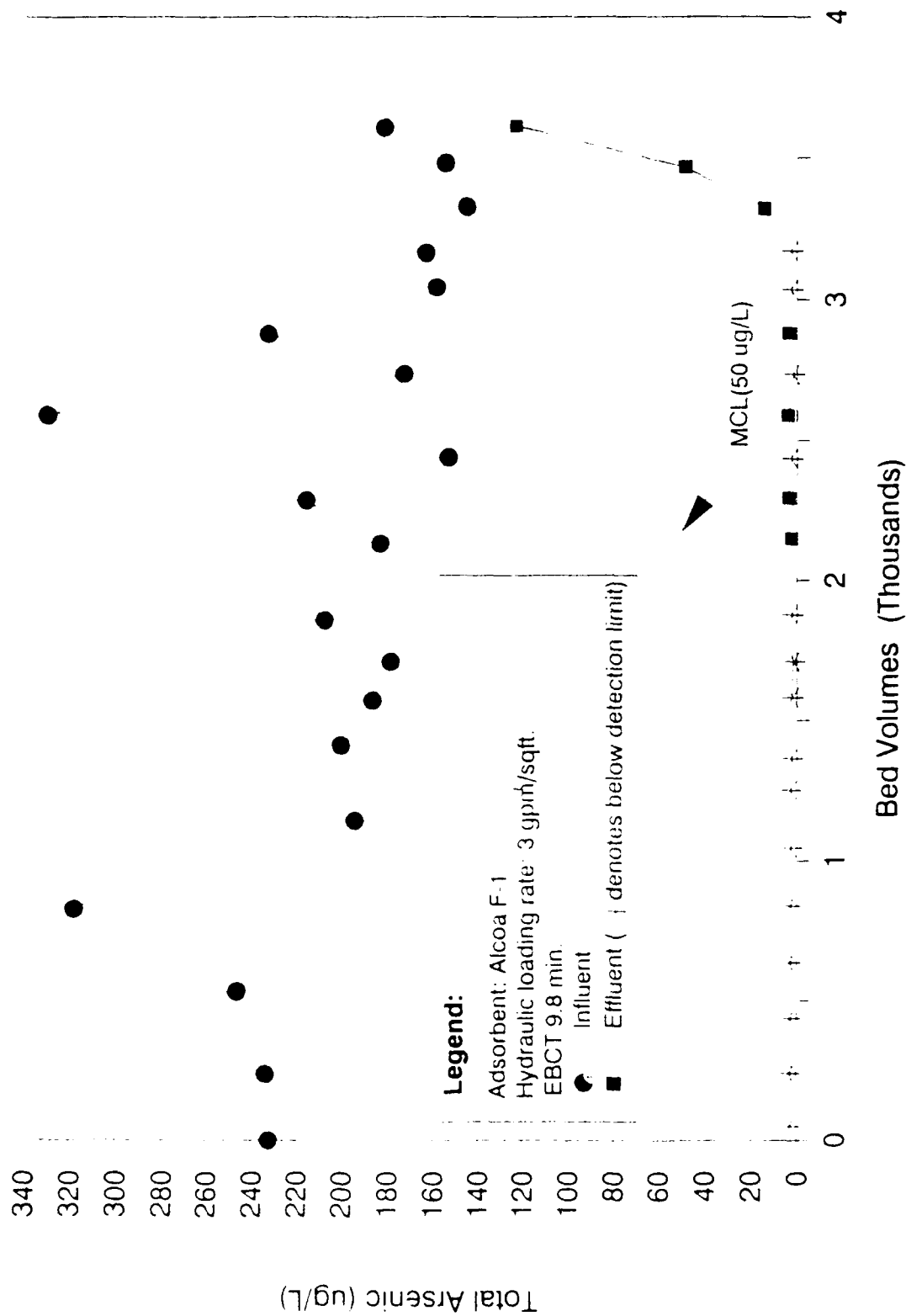


Figure 3. Arsenic removal results, Run 5b.

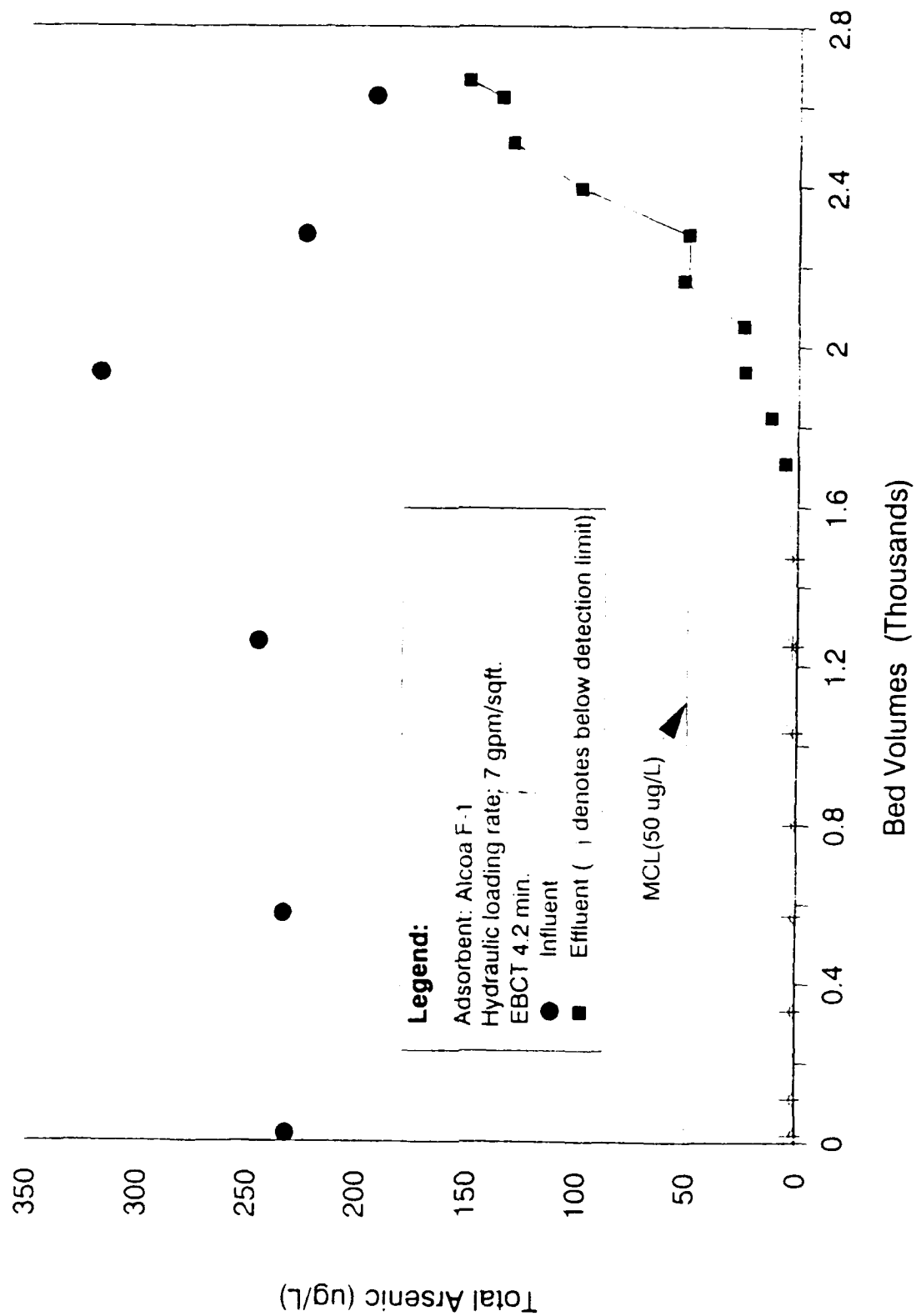


Figure 4. Arsenic removal results, Run 5c.



REHABILITATION OF MONITORING, PRODUCTION, AND RECHARGE WELLS

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ABSTRACT

Many types of water wells display significant loss of capacity due to clogging of the screen and gravel pack after being placed in service. The Waterways Experiment Station (WES) personnel, funded under a repair evaluation maintenance and restoration (REMR) work unit, have developed a procedure for cleaning water wells that can restore the capacity of clogged wells and that pushes the fouling interface further out into the aquifer than presently used procedures. Microbiological tests have shown extremely high bacterial counts correlate with an increased clogging or fouling rate and it is also known that most aquatic bacteria have a low heat tolerance. Therefore, a cleaning procedure was developed around a patented process using chemicals and heat called Blended Chemical High Temperature (BCHT). A demonstration project was conducted in conjunction with the St Louis District which concluded that well specific capacities could be increased significantly even after further conventional mechanical and "off the shelf" chemical well cleaning efforts had become economically unfeasible. The BCHT procedure is a field method that provides a minimum bacteria count in flowing wells and that also pushes the bacterial interface back out into the aquifer.

The procedure was developed initially for pressure relief wells in Corp of Engineers structures, but other types of wells critical to the operation of toxic and hazardous waste projects can be remediated and kept functional i.e., monitoring wells at waste sites and production and recharge wells in pump and treat restoration schemes. Bacterial activity near a well is not totally understood nor appreciated as to how much affect bacteria can have on site remediation in the areas of site compliance and site recharge systems. Field studies of a municipal water supply prior to cleaning revealed that iron and manganese, the metals of concern, were within the range of the mean critical level set by Ontario Ministry of Environment (MOE). All other metals were found only in trace amounts, if detected at all. It is believed that these metals and possibly organic material were bound up in the biomass because sixteen metals were detected at levels from 0.06 to 10,000 parts per million during the "waste" phase of the remediation. Following treatment the iron and manganese levels (metals of concern) returned to at or below normal. Laboratory tests have indicated that up to 90% of some organics can be removed in a flowing well through bacterial activity. Site compliance and monitoring samples should be collected in a well with low bacterial activity.

PHASE I, BIOMASS

Many types of biofouling have been reported in water wells (1,2,3). The types of fouling are dependant on the microorganisms involved. Physical and chemical parameters control the niches available for microbial growth. Existence of and competition for these niches determines the numbers and types of microbes in the fouling community. Microbial communities are dynamic. When sufficient biomass impedes a process of human interest biofouling has occurred, regardless of the "type" of microbial community. To prevent, predict or control biofouling reliably and efficiently, it is essential to understand the biofouling type. This is usually not the case as most fouling treatment is a crises management response. The types of microbes and their combinations (consortia) which participate to produce fouling are infinite. Nevertheless, their existence, life and death are controlled by the laws of thermodynamics. Energy must be obtained by biological oxidations and resultant electrons produced must be transferred to appropriate electron acceptors. Just as all human diseases do not respond equally to one treatment, nor will all fouling types. Understanding which reactions are available to the microbes and how they interact will allow scientific treatment.

A study was conducted by the US Army Engineer Waterways Experiment Station (WES), to determine biomass development versus time associated with pumped wells or pressure relief wells similar to those at Grenada Lake, MS, shown in Figure 1. The relief wells are located at the downstream toe of the dam, to relieve the uplift pressure beneath the toe of the dam. This dam was designed with relief wells and toe drains for pressure

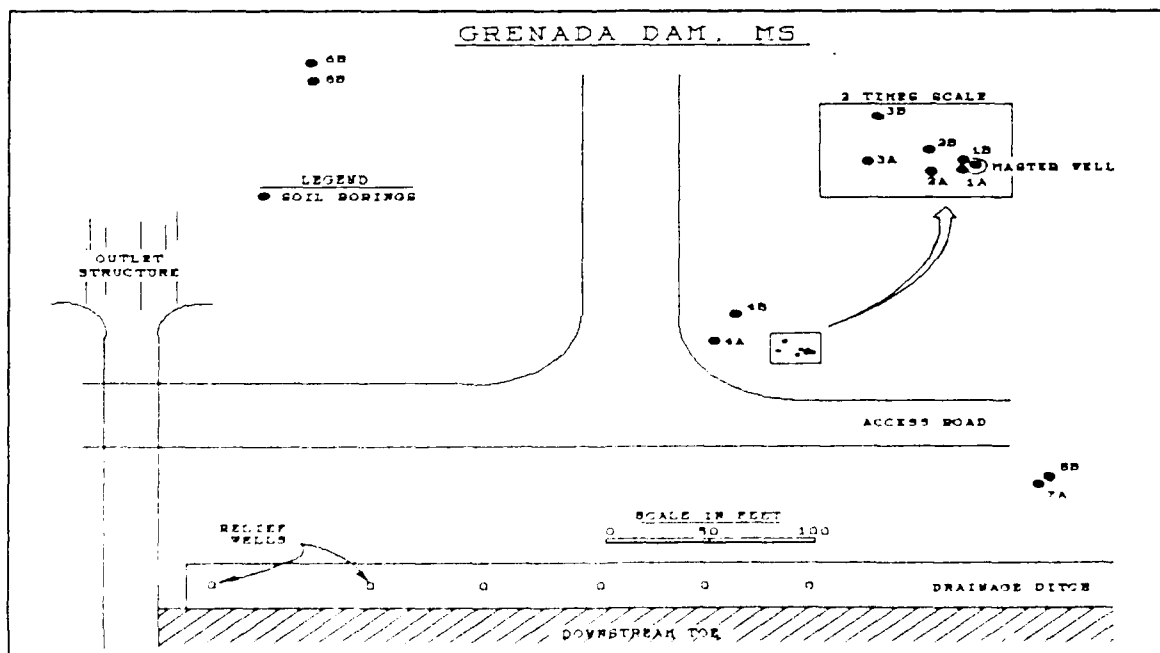


Figure 1. Grenada Dam, MS sample borings before (B) and after (A) pumping the test well

relief, and failure of the pressure relief systems can result in dam failure. The wells at Grenada have suffered chronic biofouling which has been thought to be caused by the presence of iron related bacteria. Several objectives were defined to examine this problem and affect solution(s).

- 1) Sample sediments at the base of Grenada dam for iron bacteria.
- 2) Determine the vertical and horizontal microbial density and community structure in sediments at the base of Grenada Dam.
- 3) Determine changes in microbial vertical and horizontal distribution and community structure induced by well flow.
- 4) Examine microbe types in select pressure relief wells
- 5) Design and evaluate treatment regimes for relief wells and horizontal drainage systems

MATERIALS AND METHODS

In order to enumerate the types and numbers of bacteria present in the study area, a number of methods were used and are listed below with references where applicable for more extensive descriptions:

- 1) Sanitized sampling techniques (Reference 4)
- 2) Lipid analysis (References 5 & 6)
- 3) Autotrophic bacterial enrichments (Table 1)
- 4) Iron precipitating bacteria (Reference 7)
- 5) Iron reducing bacteria (Reference 8)
- 6) Heterotrophic colony forming units (CFU) (Reference 4)
- 7) Fluorescent microscopy (Reference 9)
- 8) Scanning electron microscopy and x-ray diffraction analysis (Reference 4)

Results

Water chemistry. The water chemistry of the pumped well is depicted in Table 2. There is a high iron content (>10 mg/l) in this well. These analyses were performed under the direction of the Army Corps of Engineers Waterways Experiment Station (WES).

Autotrophic enrichments. A variety of morphological types have been selected. Fifth generation transfers have been made from Trip I. These enrichments demonstrate the loss of diversity desired in multiple transferred cultures. Many cultures contain only one or two morphological types as exhibited in Figures 2 and 3. Several additional tests are necessary to confirm autotrophy. Many different morphological forms (i.e. rods, filaments) indicate the diversity of bacteria in the sediments below the dam. They were wide-spread in their vertical and horizontal distribution.

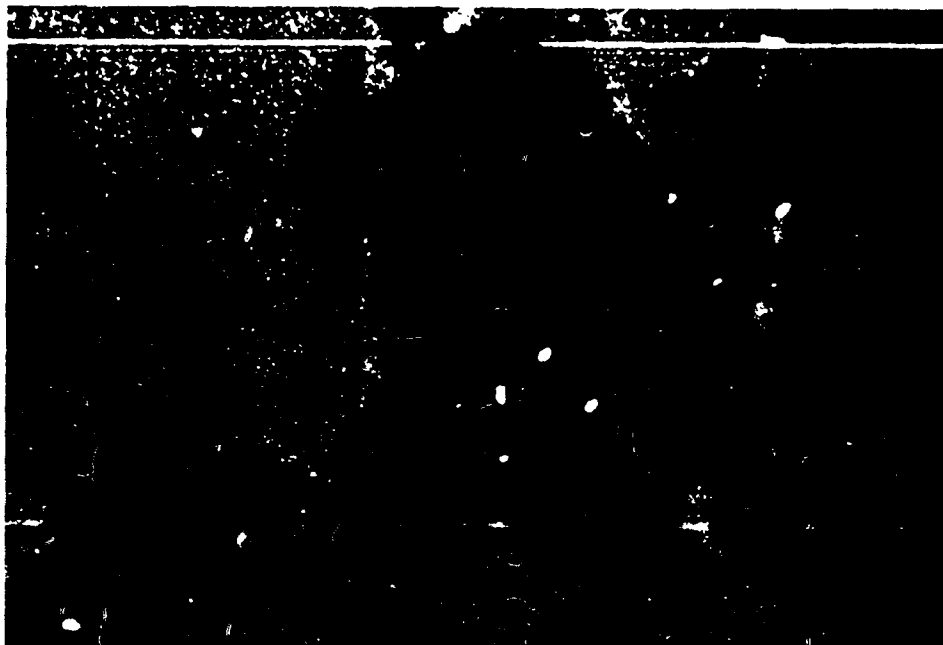


Figure 1. Epifluorescent micrograph (100x). Acridine orange stain. Fe^{2+} enrichment culture of sediment.



Figure 2. Epifluorescent micrograph (100x). Acridine orange stain. Fe^{2+} enrichment culture of sediment.

Table 1
Media types used in sediment enrichment cultures

ENERGY COMPOUNDS/ MEDIA TYPES	CULTURED BACTERIA
1) Winogradsky's	iron precipitating heterotrophs
2) acetate/ferric oxyhydroxide	iron reducing heterotrophs
3) FeS	iron and sulfur chemoautotrophs
4) Fe(HCO ₃) ₂	iron chemoautotrophs
5) Fe ⁰	iron chemoautotrophs
6) S ⁰	sulfur chemoautotrophs
7) S ₂ O ₃ ⁻²	sulfur chemoautotrophs
8) TsPepYe	oligotrophic aerobic heterotrophs

Table 2
Water chemistry data for Grenada Dam pumped well.

chemical constituents	before flow mg/l	after flow mg / l
silicon	6.3	6.8
iron	11.9	12.2
manganese	0.9	0.8
calcium	16.4	17.2
magnesium	6.8	8.0
phosphate	<0.15	<0.15
nitrate	<0.20	<0.20
chloride	6.9	6.3
alkalinity (CaCO ₃)	91.2	86.8
hardness (CaCO ₃)	69.2	75.9
total dissolved solids	130.0	137.0
total solids	288.0	290.0

Note:

specific conductance	umho/cm	umho/cm
	221	218

Iron precipitating bacteria. Seventeen isolates precipitated iron initially when grown on the modified Winogradsky's medium. Table 3 documents some characteristics of these isolates. These "iron bacteria" are diverse as demonstrated by the Gram stain, motility, cell and colony morphology. Two of these bacterial strains (1g5clfc, 1g7clfc) have lost the ability to precipitate iron from ferric citrate. Six of these isolates cannot precipitate ferric iron without citrate. One organism (1g6glfc) can precipitate Mn⁺⁺. Several of these organisms form copious slime which indicates their potential in fouling consortia.

Iron reducing bacteria. Many bacteria are capable of reducing iron heterotrophically when O₂ becomes limiting. The

TABLE 3
CHARACTERIZATION OF "WINOGRADSKY'S POSITIVE" BACTERIAL
ISOLATES FROM GRENADA DAM SEDIMENTS

ID #	COLONY DESCRIPTION TST/Fecit	GRAM RXN	Preliminary Identification
1g1a1fc	4mm, circular, entire, yellow-white, opaque metallic sheen, umbonate, depressed center	+	Coryneform
1g3d1fc	1-2mm, circular, entire, yellow, opaque <1mm, dark center irregular, rugose	-	Vibrio
1g4a1fc	4-5mm, circular, flat, entire, viscous, brown <2mm, metallic sheen	-	Pseudomonas
1g5c1fc	translucent, irregular spreading margin concentric, metallic sheen, rugose	-	Pseudomonas
1g5e1fc	3-4mm, circular, entire, convex, yellow, opaque metallic sheen	+	Coryneform
1g5e2fc	3-4mm, circular, entire, convex, yellow-white, opaque metallic sheen	+	Coryneform
1g6b1fc	2-3mm, circular, entire, clear, translucent poorly defined margin, very viscous	-	Acinetobacter
1g6d1fc	1mm, circular, entire, translucent dark center	+	Coryneform
1g6d2fc	3-4mm, circular, entire, flat, white, opaque metallic sheen, depressed center	-	Acinetobacter
1g6g1fc	rugose, dry, opaque, flesh-colored filamentous margin, metallic sheen, rugose	-	Aeromonas
1g6g2fc	2-3mm, circular, entire, yellow, translucent very viscous, metallic sheen	-	Pseudomonas
1g7c1fc	4-5mm, ovoid, pulvinate, white, translucent metallic sheen, dark center	+	Coryneform
1g7c2fc	2-3mm, circular, entire, concave, yellow dark center, metallic sheen	-	Acinetobacter
1g7e2fc	2-3mm, thin spreading margin translucent	-	Moraxella

solubilization of iron was detected as the iron became reduced in enrichment cultures inoculated with sediment sampled at a 20ft depth from all the borings. The approximate number of iron reducing bacteria was between 1 and 100/gdw by the most probable number (MPN) technique. There was no reduction of iron from cultures inoculated with sediments at depths greater than 20 ft.

Heterotrophic CFU. Figure 4 documents the number of heterotrophic microbes and their densities in relation to the pumped well. There were greater numbers of CFU in borings 2 and 6. Bacteria tended to concentrate in the shallow sediments at depths of 20 feet. Again there were a variety of these organisms as depicted by their Gram reactions, morphologies, and pigmentation (data not shown). Many of these organisms produced

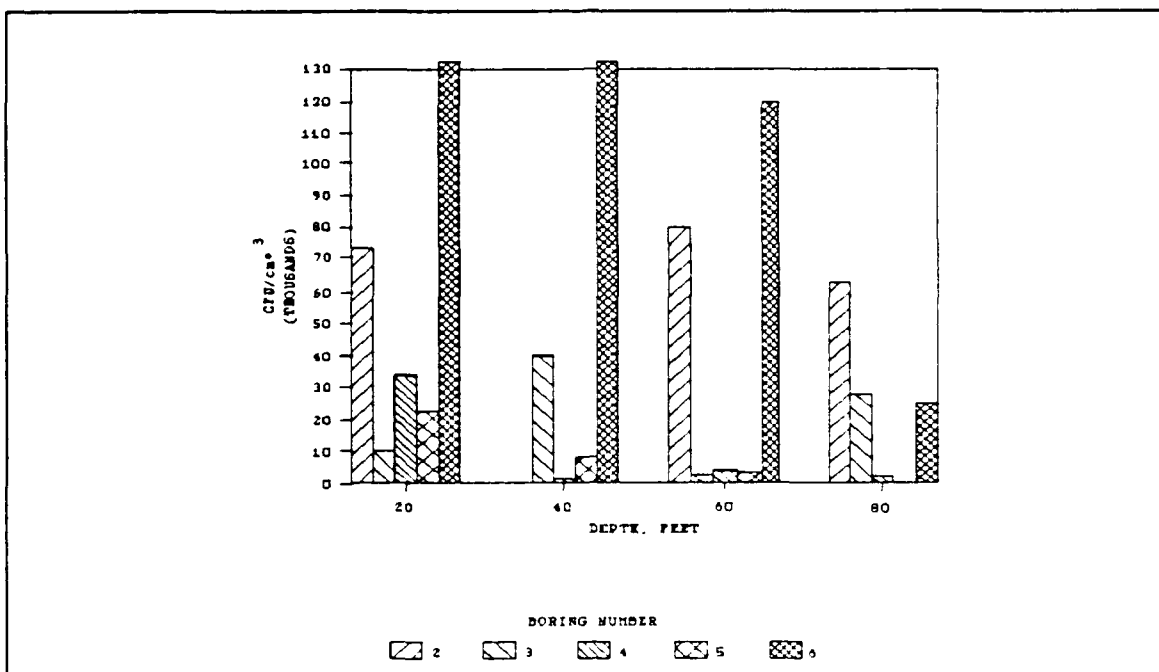


Figure 4. Plate count data (CFU) on heterotrophic medium from borings 2a - 6a; after pumping

slime on the CFU media. The sodium bentonite drilling mud which was also sampled contained $<10^3$ bacteria/gdw, as determined by spread plating onto the heterotrophic medium. These organisms

were predominately *Bacillus* sp. No organisms ($<10^1$ bacteria/gdw) were detected by the same technique in the chlorinated drilling mud. This evidence supports that these CFU represent indigenous culturable organisms. Twenty seven isolates were selected and purified from Trip I for later characterization.

Lipid characterization. Results from the phospholipid fatty acid (PLFA) analysis for Trips I and II (before and after pumping) are illustrated in the following section. Figure 5 summarizes the microbial biomass (total PLFA, pM/gdw) found in sediments with respect to depth and distance (boring No.) from the pumped well before and after pumping. Microbial biomass is concentrated in the upper 20 feet. The total quantity of biomass across the sampled area was not greatly affected by this period of pumping.

The relative bacterial contribution to sediment biomass (i15:0 + a15:0/ 16:0) before and after pumping in the sediment core at 3 ft from the well is depicted in Figure 6. The proportion of bacterial biomass increased after pumping at the sample boring closest to the pumped well (3 ft). The peak bacterial biomass, after pumping, was at a depth of 40 ft in this boring.

The eucaryotic contribution to sediment biomass

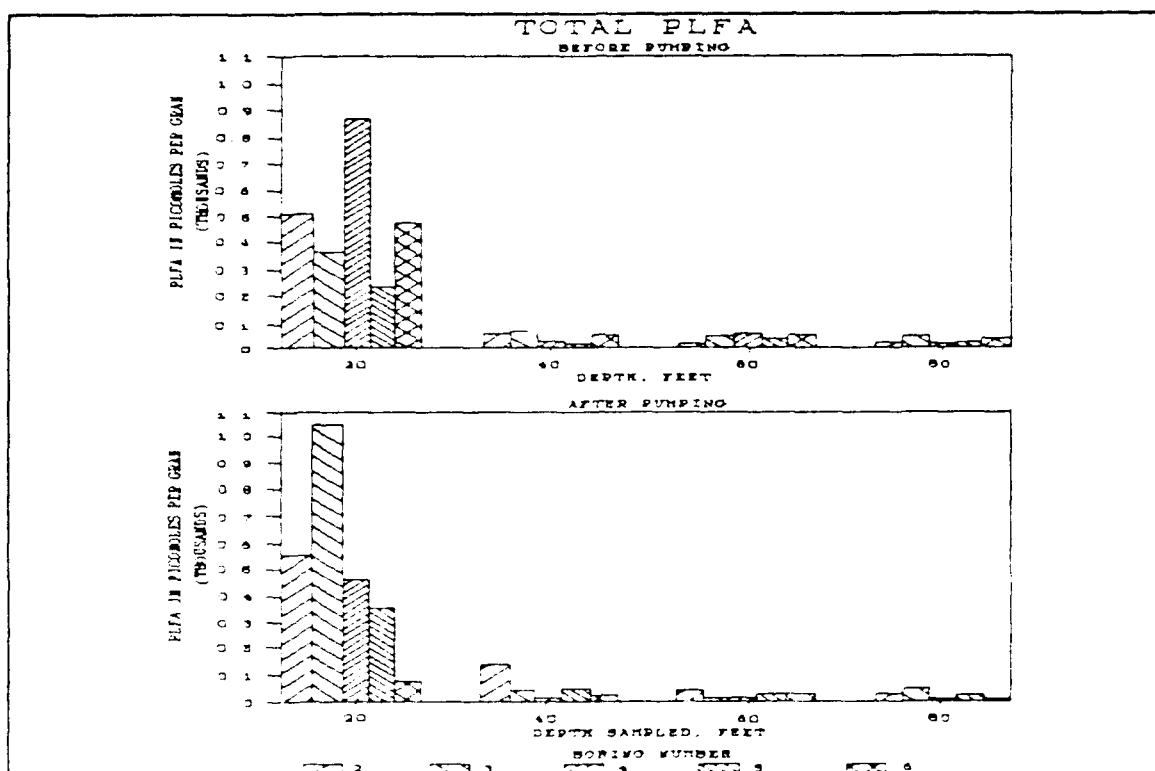


Figure 5. Microbial biomass (total phospholipid fatty acids) in the sediments versus depth and distance from the pumped well

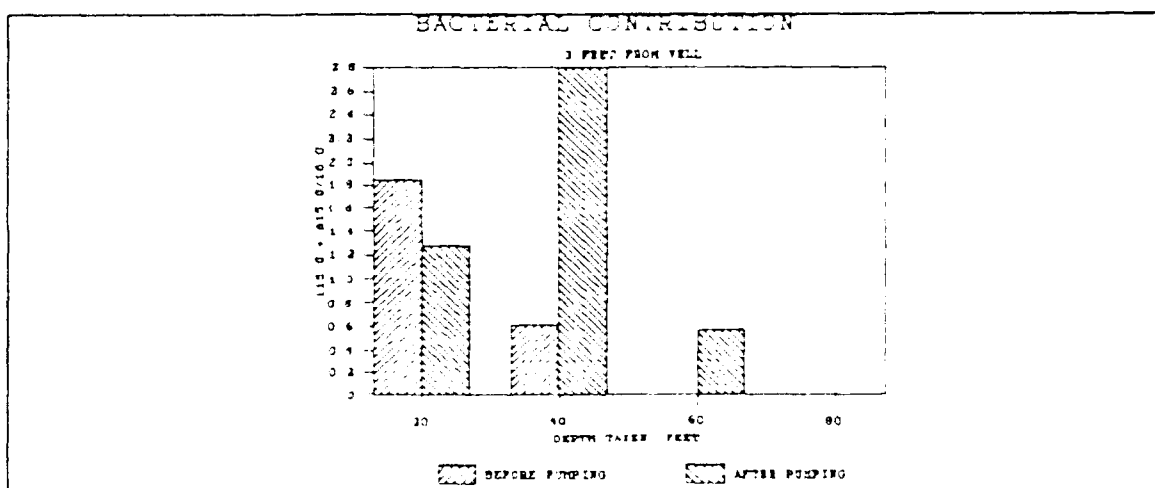


Figure 6. Bacterial contribution to sediment biomass (il5:0 + al5:0/16:0) in the sediment 3 feet from the well

(polyenoics/16:0) before and after pumping is illustrated in Figure 7. The proportion of eucaryotes increased accordingly with depth after pumping. Borings 5 and 6, farthest from the

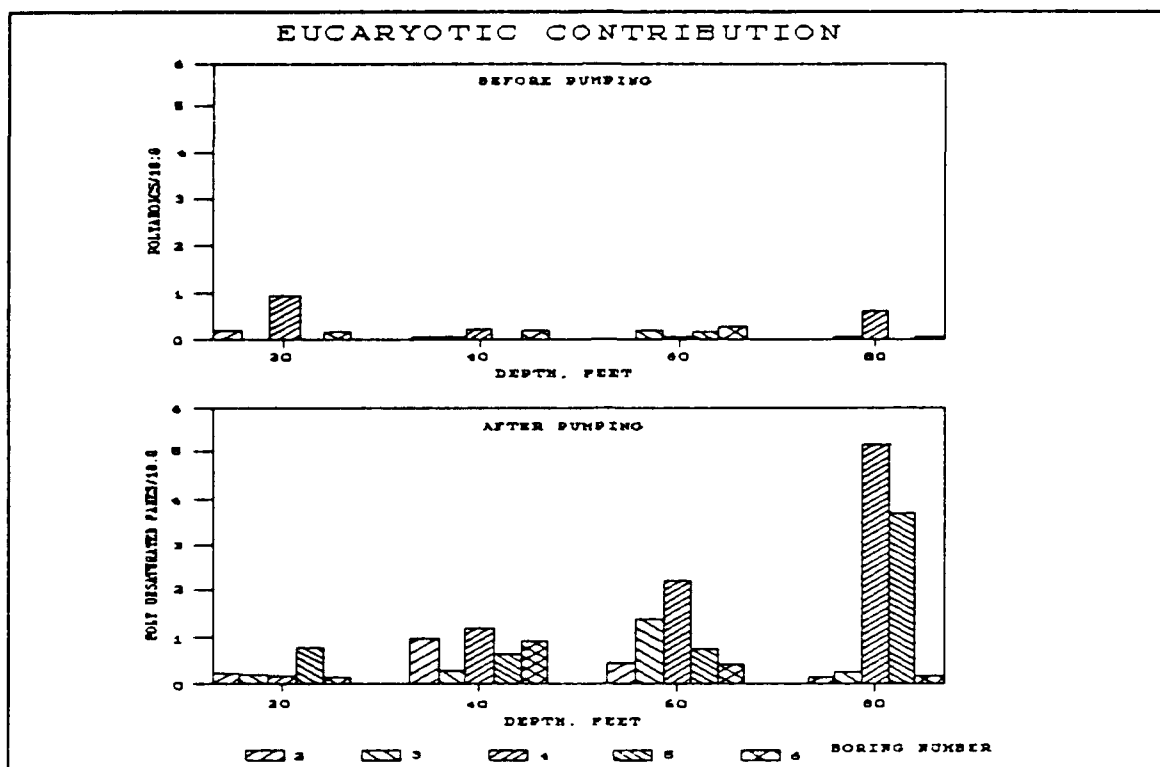


Figure 7. Eucaryotic contribution to sediment biomass (polyenoics/16:0)

pumped well, were the exception. The greatest increase in eucaryotic biomass was in the bored samples at 80 and 27 feet from the pumped well. This is illustrated in Figure 8.

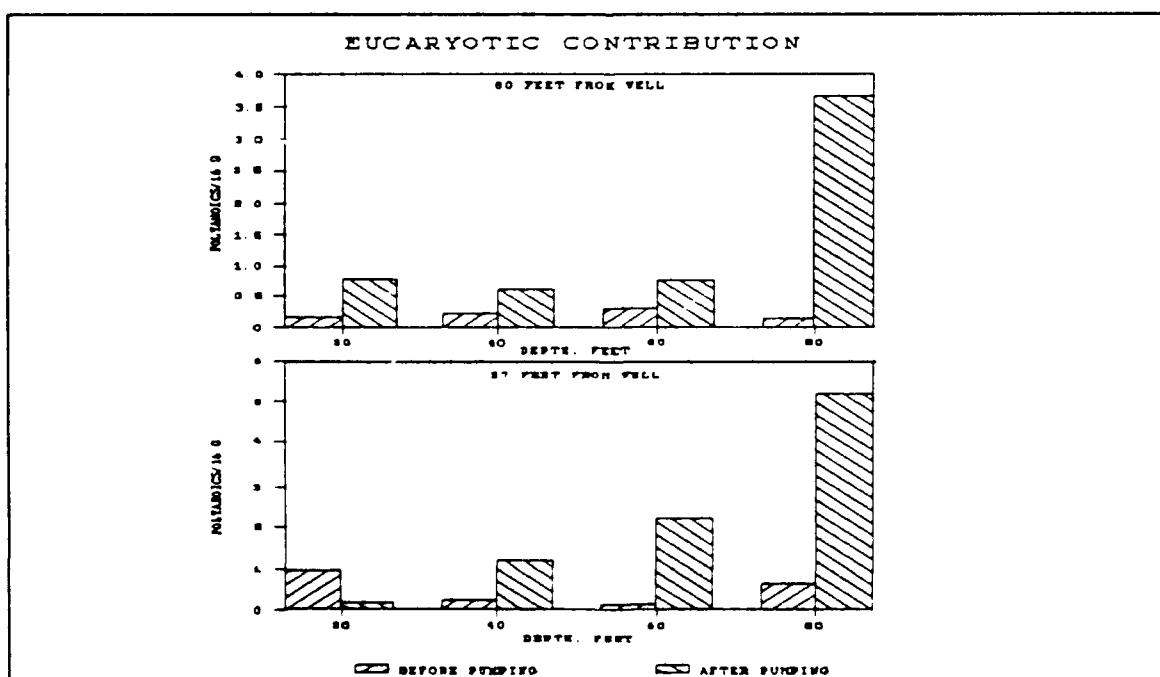


Figure 8. Eucaryotic contribution to sediment biomass at 27 and 80 feet from the pumped well

Figure 9 demonstrates lipids associated with Desulfobacter (10Me16:0) and Thiobacillus (Cy17:0). Desulfobacter is an anaerobic sulfate reducing anaerobic bacterium and Thiobacillus is a sulfur oxidizing bacterium.

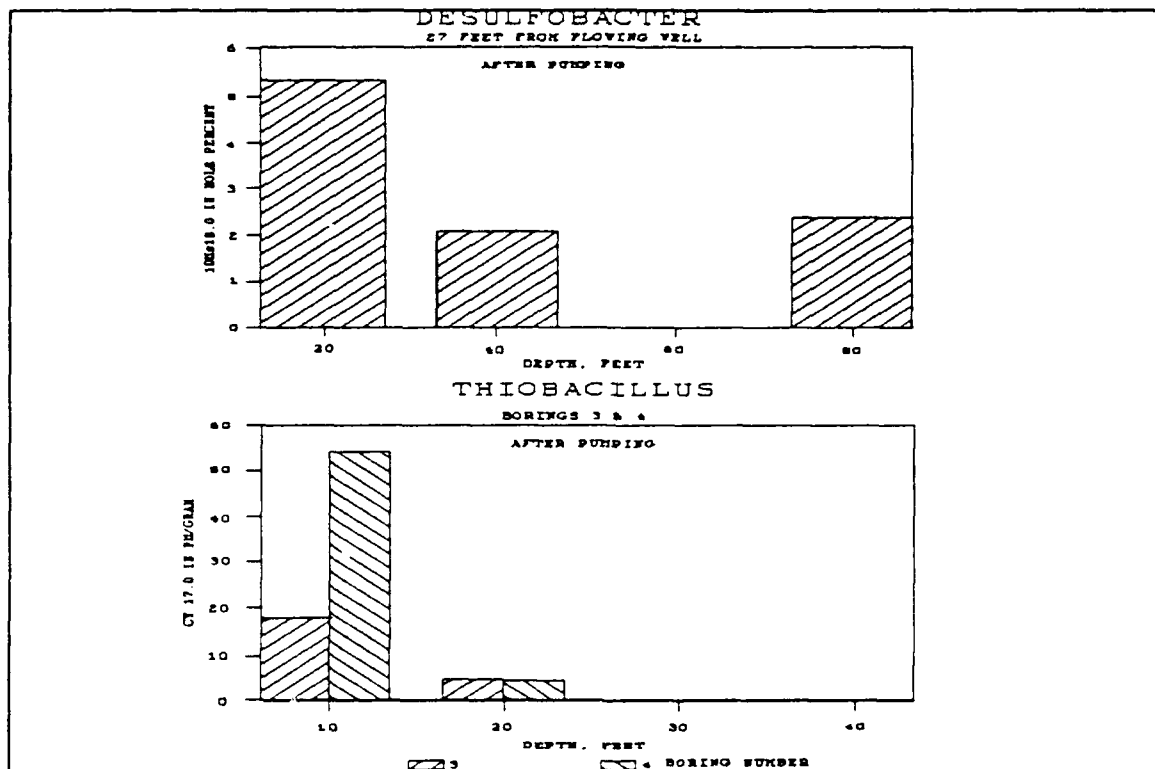


Figure 9. Lipids associated with Desulfobacter (10Me16:0, mole %) and Thiobacillus (Cy17:0, pm/gram dry weight)

Relief well microbiology. Prussian blue and acridine orange stains of bacteria from relief wells No. 2 and No. 92 (dam relief well system) are depicted in Figures 10 and 11, respectively. Scanning electron micrographs of these same wells are illustrated in Figures 12, 13, and 14. Relief well No. 2 seems to exhibit greater microbial diversity than No. 92, including a variety of filamentous bacteria and even diatoms (note frustules in Figure 13). X-ray diffraction elemental analysis of a Leptothrix filament is represented in Figure 15. This documents the iron content associated with Leptothrix sheaths.

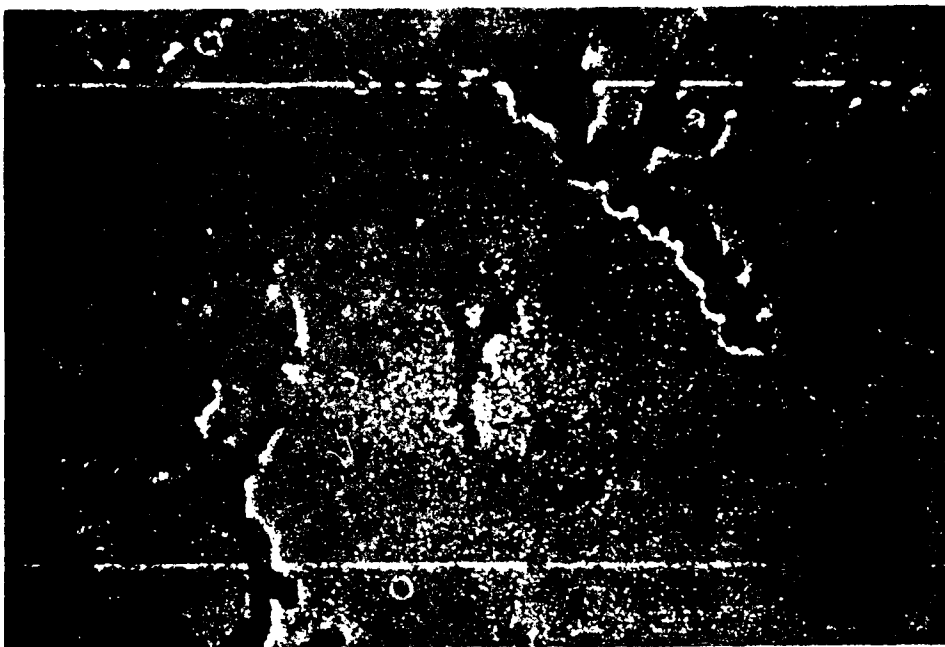


Figure 13. Light micrograph (10x) of Well No. 2. Prussian blue stain.



Figure 14. Light micrograph (10x) of Well No. 2. Prussian blue stain.

2/1/71

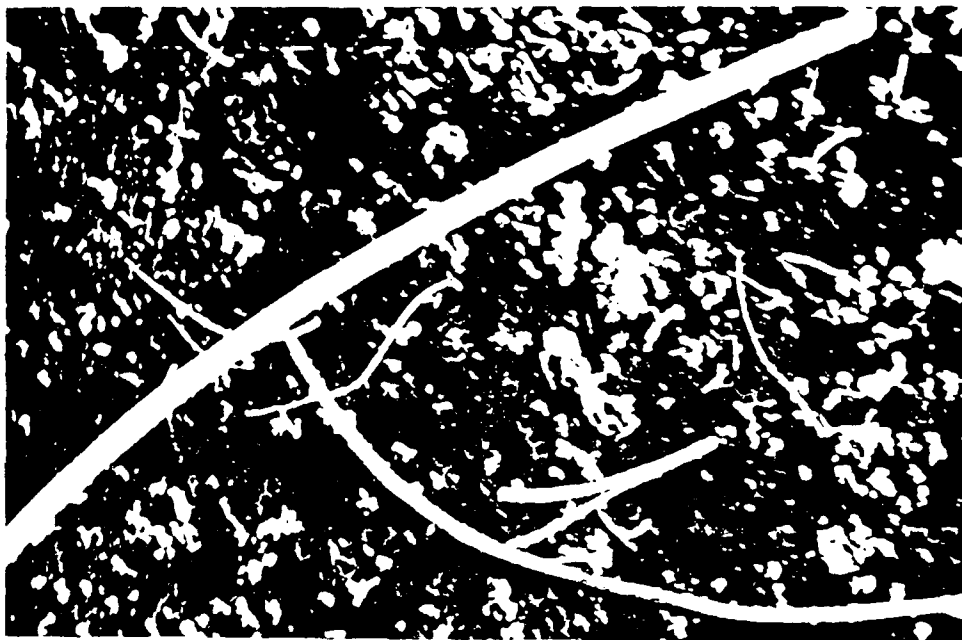


Figure 12. Scanning electron micrograph. Relief Well No. 2.

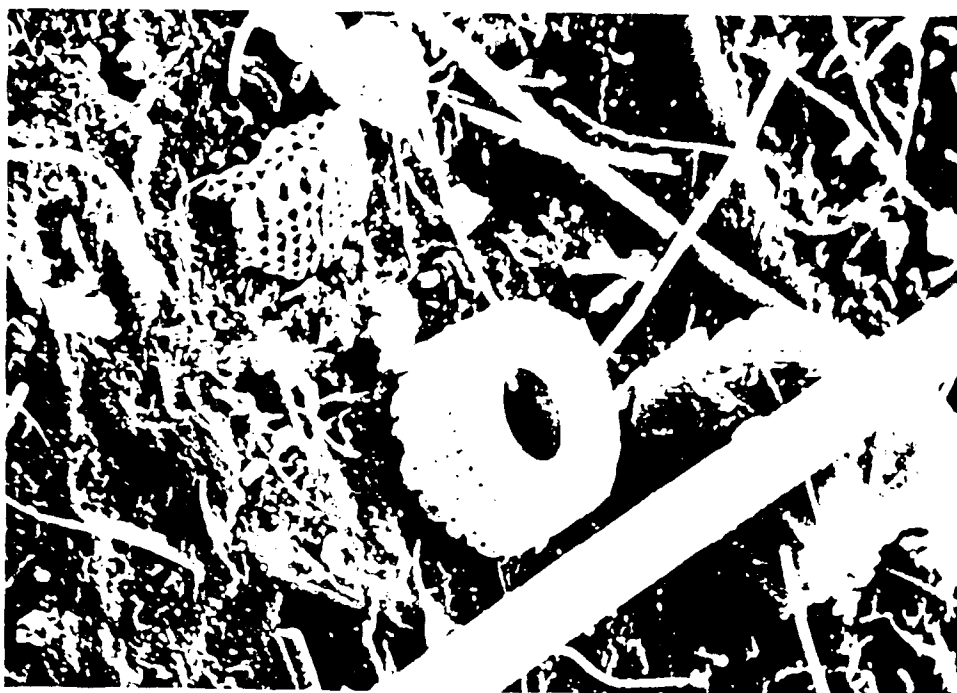


Figure 13. Scanning electron micrograph. Relief Well No. 2.



Figure 14. Scanning electron micrograph. Relief Well No. 92.

EG&G Ortec System 5000
Spectrum Plotting Program
Printplot V02.05

Sample ID: Fe bacterium AM001
Energy Range: 0-10 keV 10 eV/ch
Preset: Off
Real Time: 263.25 sec. Live Time: 230.08 sec.
17% Deadtime 7173 Counts/Second
Acquisition date: 26-Sept-85 Acquisition time: 10:08:47
Cfs 2K

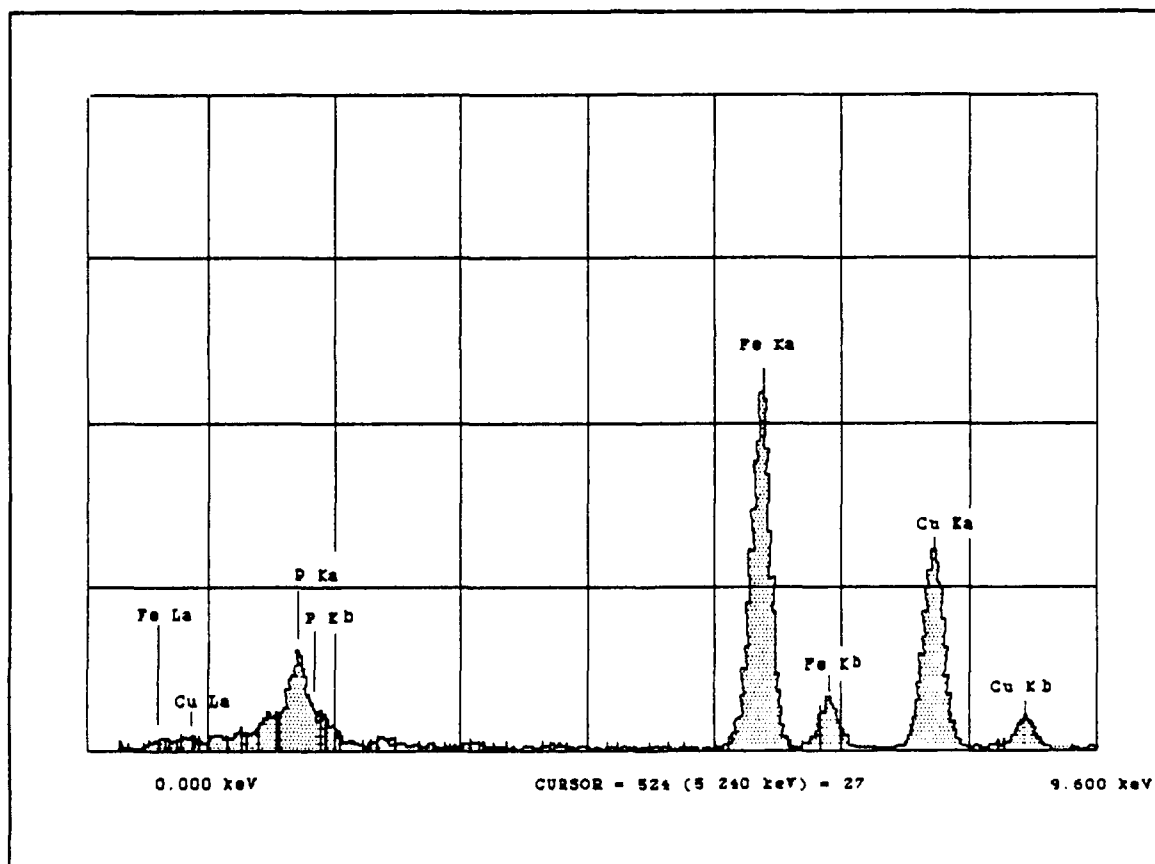


Figure 15. X-ray diffraction elemental analysis of Leptothrix filament from relief well #92

Discussion

The variety of "iron bacteria" in the sediment below the dam depicts a complete iron cycle; iron oxidizers, reducers and precipitating bacteria. Additionally, sulfur oxidizers and reducers may be present in the sediment as indicated by the presence of lipids associated with these organisms. Sulfur oxidizers have also been successfully cultured. Isolation of the anaerobic sulfate reducers was not attempted. Lipids were found which indicate the presence of *Desulfobacter*, a sulfate reducer. The higher concentrations of *Desulfobacter* fatty acids associated with shallower depths are probably due to the higher organic content of the soils as these organisms are heterotrophs. Sulfate reducing bacteria can contribute to biofouling and corrosion (2,10).

Several of the filamentous organisms seen in the relief wells by microscopy and in enrichment cultures remain unidentified. *Gallionella* was identified and is a proven chemoautotroph. Other chemoautotrophs such as *Thiobacillus* are not morphologically distinct but may be equally important in determining the type of fouling at Grenada Dam. To determine if the ferrous iron can support an autotrophic community, further dilutions of these autotrophic cultures are being conducted. Each subsequent dilution removes organic carbon that obscures results. The concept of mixotrophy resolves that organisms, such as *Sphaerotilus* and *Leptothrix*, are capable of oxidizing organic and inorganic constituents. This may or may not be coupled to energy yielding reactions.

The predominance of autotrophy to heterotrophy as an energy source for microbial productivity is relevant to the fouling problem. The concentration of iron in the water analysis of the pumped well suggests that there is sufficient reduced iron to support chemoautotrophic bacteria. However, there is much less energy available from oxidation of inorganic compounds than from organic substrates. Additionally, many of these organisms fix carbon dioxide which suppresses growth efficiency. Energy obtained from chemoautotrophic reactions may limit fouling quantities of growth to high water velocity areas. The diffusion of oxygen is also imperative for these reactions to occur. Heterotrophs, dependant on organic carbon excreted, would grow in conjunction with these organisms. This environment would occur in proximity to the well so that the fouling would be restricted to that immediate area. In some relief wells horizontal flow may exceed vertical flow, so that "non-flowing" relief wells may be fouled by the same mechanism. Treatment and cleaning of these wells might be effective on a relatively small area. The bad news is there is a tremendous potential for regrowth or seeding of these organisms at the Grenada Dam site. Distance of biocide peratration would control the time required for regrowth.

A complete water chemistry analysis including concentrations of ferrous, ferric iron, sulfide, sulfur, sulfate, nitrate,

nitrite and dissolved organic carbon, is needed from several relief wells and the pumped well. This would allow further elucidation as to the energy mechanisms available to the microbial communities at these sites.

Reduced forms of iron and sulfur may be produced by heterotrophic consumption of organic material in the oxygen limited sediments in the lake bed behind the dam. This would impact the communities associated with relief wells at this site and others.

There are high numbers of heterotrophic bacteria in the sediments surrounding the dam. The higher proportion of culturable bacteria CFU:PLFA at boring 6 could illustrate the input of organic carbon from the adjacent spillway. As the sediment in this area would be more eutrophic, a higher proportion of these organisms would be able to produce CFU.

A very taxonomically diverse group of heterotrophic bacteria were found to precipitate iron. These "iron precipitating bacteria" were ubiquitous in these sediments.

Data from Trips I and II suggest that flow increased the relative bacterial population in the boring closest to the pumped well. This biomass was maximum at the 40ft depth. This could be due to increased vertical flow. The CFU data from boring 2 after pumping also indicates a higher bacterial biomass relative to borings 3,4,and 5. PLFA in boring 6 are at variance with CFU data. Boring 6 demonstrated among the lowest PLFA concentration and the highest CFU.

There was a high proportion of eucaryotic biomass in these samples from Grenada dam. Eucaryotes, microorganisms with a membrane bound nucleus, include fungi, algae and protozoa. Some fungi and molds were found in the sediment samples plated onto the heterotrophic medium. This medium is not designed for optimum growth of fungi and their numbers were not significant compared to bacterial CFU. Protozoa from aquifer sediments are currently being isolated and characterized by Bill Ghiorse (personal communication). They may be important predators of bacteria in sediments and some have suggested that they may be used to control bacterial biofouling.

The microscopic examination of two relief wells reveal entirely different microbial communities. Relief well No. 92 was predominately Leptothrix sp. A sample from relief well No. 2 was very diverse exhibiting several types of filamentous bacteria including Gallionella sp. This illustrates the potential for markedly different fouling types in the relief wells across the dam face. This may be due to: 1) velocity of flow. This would be evident if a redox gradient is discovered across the dam face. PLFA patterns would demonstrate similarity by proximity. 2) variable geology thus water chemistry. As the old river meandered, deposits would be irregularly lain across the area

which is now the dam foundation. There would be variability in the well water chemistry and resultant microbial communities and little correlation between well proximity. 3) sampling error. This observation could be at fault due to sampling error. The material could have come from a different depth of the well and there may be a vertical gradient of organisms on the well screen. This possible sampling artifact will be studied by video camera review of the well in the Phase II study.

The general lack of viability of relief well bacteria, indicated by the nucleotide stain acridine orange, is evident in Figure 11. Very few of the bacteria illustrated by light and electron microscopy in Figures 10, 12, 13 and 14 may be alive. For treatment to be effective in these wells, the dead mineral encrusted filaments must be removed physically, or in some cases, filaments might wash out by natural water flow. It is evident that filamentous mineral encrusted bacteria will physically plug a well. We do not know the age or longevity of these filaments after death, however they may be resistant to natural degradation.

FOULING LOCATION

The location of the biofouling, as discerned by the excavation of the Grenada, MS well, was concentrated vertically at the top of the screen and horizontally at the gravel sediment interface. This area could provide a high flow, a pressure drop at the sediment/gravel pack interface, oxygen diffusion from above, and nutrients from the adjacent sediment. A similar observation occurred from the excavation of a fouled injection well at a hazardous waste treatment facility (21). The microbial biomass was maximal at the same relative location. In this case, the situation was complicated by the precipitation of carbon fines "leaking" from the granular activated carbon treatment system.

It is uncertain what proportion of biodegradation occurs in injection or recovery wells associated with biofilms. It is probable that this biomass is dependent to some extent on organics in these waste for carbon and energy. Through proper design, the location and extent of the biomass might be controlled. Under these circumstances, the microbes involved could represent a resource in insitu treatment rather than a fouling hindrance.

Further implications of biofilms could extend to monitoring wells. Work by Dr. Roy Cullimore of Canada has shown that a basic iron related biomass can remove as much as 90% of some organics when the organic is passed through the medium. Microbes and their enzymes can catalyze reactions in microseconds, so that water quality reported from monitoring wells could represent artifacts of adjacent microbial activity.

Microorganisms will form biofilms associated with water

wells. It is critical that we understand the processes whereby growth is encouraged so that: (1) biofilms will not develop to the stage of biofouling and (2) treatment regimes can be optimized to provide remediation at the location of fouling. The latter must occur if cost effective water well maintenance and rehabilitation are to become a reality.

Conclusions

- 1) Bacterial groups associated with biofouling are ubiquitous in the sediments surrounding Grenada Dam. Treatment regimes relying on initial kill plus cleaning and disregarding inhibition may not be effective due to rapid reseeding or reinoculation of the well area.
- 2) Iron is available in high concentrations and organisms have been identified and cultured, therefore, chemoautotrophy may be energetically important at the Grenada dam site. Energetics of these organisms suggests that they may be restricted to the immediate well area. Treatment penetration area may be less important than frequency (see conclusion 1).
- 3) Water flow into the well represents a fortuitous input of energy and potential electron acceptor, oxygen. Under these conditions all wells age toward a finite lifetime and the rate may be controlled only by an effective rehabilitation treatment.
- 4) Initial examination of relief well microbiota reveals diversity in the microbial community structure between wells. Treatment regimes may not exhibit equivalent effectiveness (i.e. % recovery) in all wells.
- 5) Relief well fouling material may be predominately dead microbial cells and precipitated minerals. Cleaning methods which cause dissolution of these plugs should be used.

PHASE II, METALS

In our investigations to determine the effectiveness of the RCHT procedure, one sample was taken for metal analysis during the final stage of surging and pumping from a well in Armstrong, Ontario. The results of this sample analyzed by the Ontario Ministry of the Environment (MOE) are presented in Table 4. Prior to cleaning the well, the only metals of concern were iron and manganese which were in the range of the MCL set by MOE. It is interesting to note the variety of metals recovered, including those with established toxicities. The recovery of metals from the cleaning process represents circumstantial evidence of biofouling involvement in metals concentration.

Table 4
Metals Analysis*

<u>Metals</u>	<u>Concentration, ppm</u>
Copper	9.7
Nickel	0 .45
Lead	2.0
Zinc	9.7
Iron	10000.0
Manganese	24.0
Aluminum	55.0
Barium	3.8
Beryllium	0.06
Cadmium	0.26
Cobalt	0.75
Chromium	0.508
Molybdenum	1.0
Strontium	0.4
Titanium	3.0
Vanadium	0.8

*Determined by the Ontario Ministry of Environment
on a pump to waste sample

At Grenada, when the fouling material from relief wells was subjected to light and scanning electron microscopy (SEM), the majority of the filamentous bacteria involved appeared to be *Leptothrix*, as shown in Figure 14. When these filaments were analyzed by x-ray diffraction, the predominant metal signal was identified as iron. This represents conclusive evidence that metals were precipitated from the flowing waters by microorganisms and this was not an abiotic process.

In laboratory studies, the capacity of an iron related bacterial isolate to precipitate iron from the citrate chelant was demonstrated. A two week incubation time allowed certain isolates to totally clear the medium of the golden color representing the ferric citrate complex.

Admittedly, the precipitation of metals is the most notable visible evidence of biofouling especially with regards to "iron bacteria." The bright red ochre of these bacterial masses is quick to catch the eye, however, the bacterial and chemical processes involved are complex and not homogenous from site to site. Bacteria catalyze the precipitation of metals by a variety of mechanisms. Some of these reactions are fortuitous, others are essential to the metabolism and life of bacteria involved. No doubt accumulation of metals within the biofouling mass results from a combination of factors discussed below.

Fortuitous reactions. Fortuitous reactions include ORP/pH shifts and chelant degradation. Changes in ORP/pH may result from the production of some reduced product (e.g., the production of sulfide by sulfate reducing bacteria), consumption of oxygen by aerobes or, the production of an acidic metabolite.

Transition metals often exist in different ion forms in the environment. The ion form is related to the pH/ORP. Solubility, toxicity and bioavailability all can be effected by ion form, so that it is evident that the importance of microbe/metal interactions extends beyond the realm of fouling and metals precipitation.

Chelant degradation is doubtless important in the environment, however, the quality and quantity of naturally occurring chelants is poorly understood. Citric acid is one such chelant. When combined with ferric iron, the complex is soluble. Ferric citrate constitutes the basis of one of the more common bacteriological tests for the iron related bacteria, or Winogradsky's medium. Citric acid represents a carbon and energy source for a variety of bacteria (this paper and 11). As the citric acid is catabolized, the complex becomes unstable and ferric iron precipitates. Very little of the iron is needed by the cells so that the majority is precipitated outside of the cell. Other Di- and tri- carboxylic acids may act as natural chelants such as oxalate, fumarate, malate and succinate. Additionally, other metals may be solubilized by these chelants including aluminum (12) and uranium (13). It could be that some of these processes are involved in the concentration of metals associated with fouling mass.

One other category of a fortuitous metal/bacterial interaction involves the non-specific binding of metals to bacterial structural components. These components include bacterial cell walls, glycocalyx (including capsules), and the outer membrane of Gram negative bacteria (14, 15, 16). To illustrate the versatility of this mechanism, the cell wall of *Bacillus subtilis* exhibited the capacity to bind 127 different metals (17).

Metal metabolism. Bacteria often exhibit a requirement for a variety of metals. This includes catabolic processes where metals are oxidized for energy, or reduced as electron acceptors. The oxidation of metals is most notably represented by *Gallionella*, which depend on for their existence: oxidation of ferrous, soluble iron to produce ferric insoluble iron. This ferric iron is excreted as long "tails" which contribute to the fouling mass (18). Iron reducing bacteria represent a relatively "new" category of bacteria which use iron as an electron acceptor, much as man and aerobic bacteria use molecular oxygen (19). In performing this process, iron is solubilized to the ferrous form. These processes can be worrisome if toxic metals become mobile in the aquifer.

In addition to electron donor/acceptor reactions, a variety of metals are required by bacterial cells as cofactors in enzymes. A partial list includes iron, nickel, chromium, zinc, vanadium, molybdenum, copper, and manganese. It is also interesting to note that several of these metals are highly toxic to humans. Since these metals are requirements and as such are

essential to the life of the bacteria involved, a variety of mechanisms for their acquisition have evolved. Siderophores represent the most well understood example of acquisition (20). Siderophores are peptide chelants produced by cells which have such a high affinity for iron they can dissolve the ferric state of iron which is very insoluble. Once in solution, the bacteria recover the iron/siderophore complex by utilizing specific cell receptors. There are a variety of these complexes, so that the cell will seek to selfishly recover their own.

PHASE III, TREATMENT

The conclusions of the Phase I study indicated that a well rehabilitation method was needed that would provide initial kill of the active bacteria in the well, dissolve the biomass in the screen, in the gravel pack, and some distance into the aquifer, and some inhibition of future growth. A redevelopment procedure was developed using a patented process known as the Alford Rodgers Cullimore Concept (ARCC). The procedures in general include an initial well diagnosis performed with a prepackaged field microbiological test kit (BART kit) which is designed to give a qualitative indication of the types of bacterial and chemical agents at work in the wells, and a very general indication of the bacterial concentrations. The initial water chemistry is also measured prior to treatment. A treatment is then designed with the information from the tests, targeting the problematic agents with an appropriate set of chemicals.

Redevelopment of the wells using the ARCC method is based on the use of blended chemicals and high temperature (BCHT) and is divided into three principle elements of treatment:

a. Shock. This phase is achieved by adding high temperature chlorinated water to the well and surrounding aquifer to "shock" kill or reduce the impact of deleterious algae and bacteria. The water is chlorinated to >700 ppm with gaseous chlorine to avoid binders found in powdered chlorine and is applied to the well as steam until the well temperature is brought above 120 deg F for massive bacterial kill. The chlorine treatment remains in the well for a specified period of time; mechanical surging is used, followed by removal by pumping of the initial loosened biomass.

b. Disrupt. This phase is achieved by the addition of chemical agents, acids and surfactants, and steam to the well and surrounding aquifer while the well is pressurized. Mechanical surging to break up organic and mineral clogging in the system is also used. The mechanical surging and chemical set time are important during this phase to cause dissolution of the remaining biomass.

c. Disperse. This phase of treatment consists of removal

of the material that has been clogging the well and aquifer. Acceptance criteria for the well are checked and further cycles are considered or a final cold chlorination treatment is applied for inhibition of any remaining bacterial colonies.

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Air Stripping of Contaminated Groundwater - How Much Does It Really Cost?

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Abstract

An integral part of the U.S. Toxic and Hazardous Materials Agency's (USATHAMA) technology transfer effort is to perform economic analyses of processes developed for remedial actions or currently in use in remedial actions. Accordingly an economic evaluation has been performed on three existing groundwater air stripping facilities: Twin Cities Army Ammunition Plant (TCAAP) in Minneapolis, Minnesota; Letterkenny Army Depot (LEAD) in Chambersburg, Pennsylvania; and Sharpe Army Depot (SHAD) in Stockton, California. An evaluation was performed at each site to determine the capital costs for the existing facilities, determine the operating cost for the existing facilities, and identify significant cost factors for each of the facilities. Because of the different locations and demands placed on the units, the three facilities vary considerably in design and operating philosophy. The size of each unit ranges from 200 gal/min at LEAD to 2900 gal/min at TCAAP. The TCAAP and LEAD units are located in cold climates and require extra freeze protection, while the unit at SHAD is essentially in the open. The unit at LEAD also contains liquid- and vapor-phase carbon adsorbers to further reduce the VOC emissions; this was found to be a major cost item from both a capital and an operating standpoint. Operating personnel requirements varied at each facility as did materials of construction.

Introduction

Air stripping represents controlled contact of a liquid containing volatile contaminants with a clean stream of air. Ideally, the entire volatile component is transferred from the liquid to the air/vapor phase. In a liquid-vapor contactor, such as a packed-column air stripper, the mass transfer rate from liquid to vapor is controlled by the equilibrium concentration of the compounds in the water and the air at the specified conditions. This mass transfer capability is represented by Henry's Law constant of each compound in the liquid and gaseous phases.

Economic studies have shown that air stripping is recommended as the most cost-effective method for treating groundwater contaminated with VOCs. Air stripping offers effective VOC removal at reasonable capital and operating costs. Air stripping is probably the most common method used in removing

VOCs from groundwater, especially where the groundwater contamination involves low solvent concentrations (in the ug/L range) and in areas of the country where the treatment facility is located in remote locations. Under these conditions, air stripping is favored since VOC-laden exhaust air can impact on ambient air quality. When effluent water quality is critical, multiple air strippers (in series) can often be used to remove VOCs below detectable limits.

Carbon adsorption can also be used in conjunction with air stripping to remove VOCs from the groundwater; however, this method is much more expensive than air stripping alone. Carbon adsorption, although highly effective, is not normally used unless the influent water quality is such that air stripping by itself will not purify the water.

As part of the U.S. Army Toxic and Hazardous Materials Agency's (USATHAMA) technology transfer effort an economic evaluation has been performed on three existing Army groundwater air stripping facilities: Twin Cities Army Ammunition Plant (TCAAP) in New Brighton, Minnesota; Letterkenny Army Depot (LEAD) in Chambersburg, Pennsylvania; and Sharpe Army Depot (SHAD) in Stockton, California. The purpose of this evaluation was to determine the capital costs for the existing facilities, determine the operating cost for the existing facilities, and identify significant cost factors for each of the facilities. The work reported on in this paper was performed by the Tennessee Valley Authority National Fertilizer and Environmental Research Center under contract to USATHAMA.

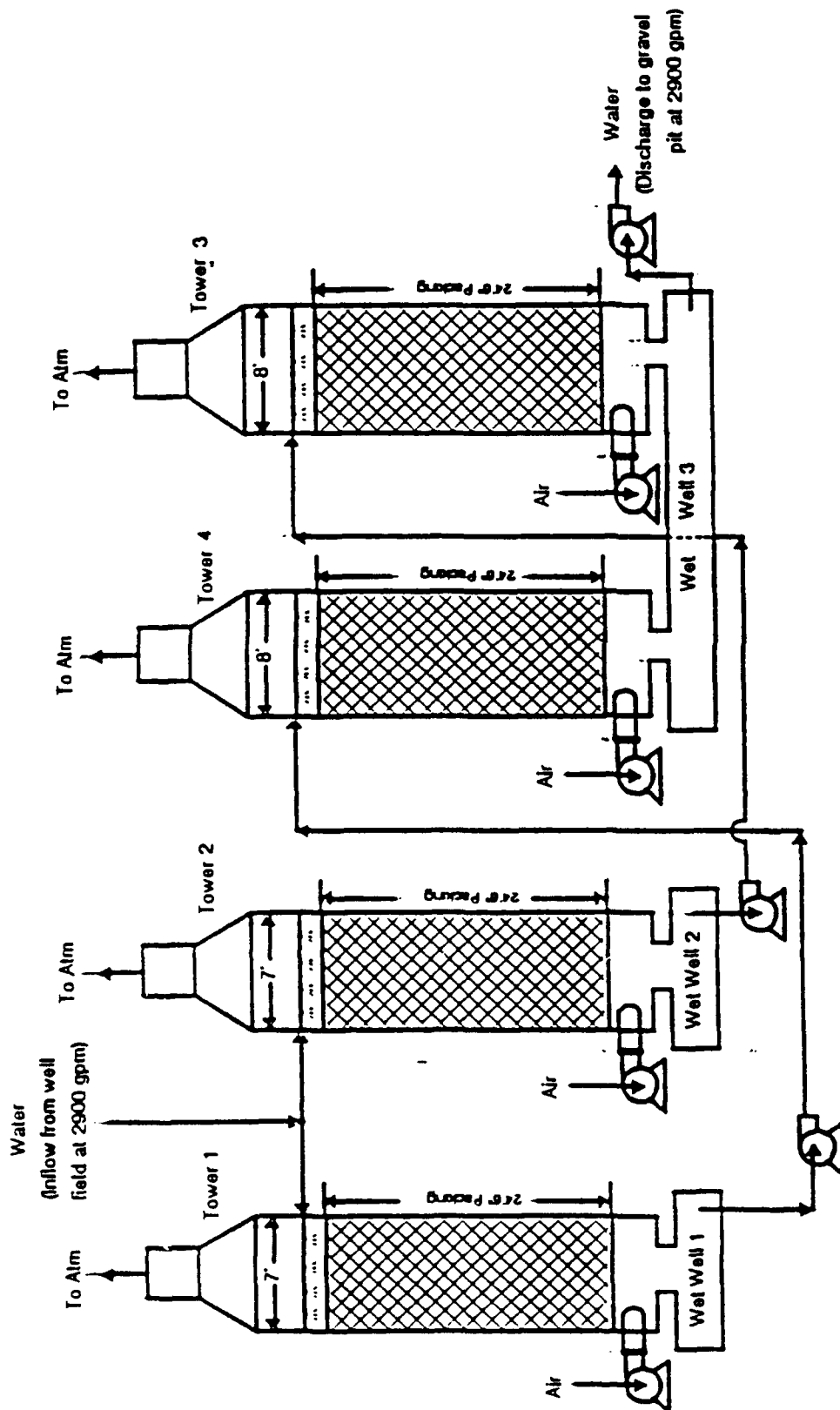
Site Descriptions

TCAAP

TCAAP was constructed in 1941 and 1942 for the production, inspection, and storage of ammunition. In later years the handling and storage of strategic and critical materials for other Governmental agencies was added to the mission. Studies have shown that underground water aquifers at TCAAP are contaminated primarily with trichloroethylene (TCE) and a variety of its breakdown products. Most of these VOCs can be traced to the methods of disposal of explosives, solvents, oil and other organic materials at TCAAP. In an attempt to properly remediate the underground aquifer at TCAAP, it was decided that the most cost-effective method would be to build a water treatment site which employed packed column air strippers.

The water treatment site at TCAAP consists of four air strippers which are operated on a continuous basis to process approximately 2,900 gallons/minute (gal/min) of water. Figure 1 is a flow sheet of the process. The towers are enclosed in a heated metal building to a height of eight feet; the remaining portion of the towers extend through the roof of the enclosure. Each tower has a total height of 34 feet and an effective





Flowsheet of Water Treatment Plant at Twin Cities Army Ammunition Plant

FIGURE 1

packing height of 24.5 feet. The towers are constructed of carbon steel. The associated piping with the towers is ductile iron. Towers 1 and 2 are both seven feet in diameter while towers 3 and 4 are eight feet in diameter. The four towers serve to make up two trains which operate in parallel; towers 1 and 4 operate in series and towers 2 and 3 operate in series. A 16 inch diameter inlet water line to the treatment plant carries about 2,900 gal/min to the plant. Once the water supply enters the enclosure, it splits and the lines reduce to 8 inches in diameter and carry 1,450 gal/min of water to towers 1 and 2. Water exiting tower 1 enters a wet well. From this wet well the water is pumped to the top of tower 4 for its final scrubbing. Water from tower 2 enters a separate wet well and is pumped to the top of tower 3 for final scrubbing. The clean water from towers 3 and 4 is mixed in a third wet well. All three wet wells are 20 feet by 20 feet by 8 feet in size. The water from the third wet well is pumped through a 16 inch diameter line to a gravel and sand pit where the water is allowed to reenter the underground water table. The gravel and sand pit is located onsite, about 5,300 feet from the water treatment facility.

Towers 1, 2, and 3 all use three inch Intalox saddles for packing, while tower 4 uses three inch lanpac. Each tower has its own separate blower. The blower capacity for towers 1 and 2 is 5,100 cubic feet/minute (ft^3/min) of air. The blower capacity for towers 3 and 4 is 9,850 ft^3/min . For towers 1 and 2 the air:water mass ratio is 25:1, while for towers 3 and 4 the air:water mass ratio is 50:1.

The contaminated water is pumped to the treatment site from 12 boundary wells and 4 source control wells within the installation. Each well has its own separate pump which is totally enclosed for cold weather protection. The typical pumphouse is constructed of eight inch concrete blocks and is about eight feet by 13 feet in size. The forcemain system is constructed of six to 16 inch ductile iron piping and is installed in a trench seven feet underground.

The plant is equipped to operate automatically with little need for constant staffing of personnel. An operator normally makes routine visits to the plant once each day. The operator will spend approximately one hour at the site checking the system, recording meter readings, and making minor repairs.

LEAD

LEAD was established in 1942 with the primary mission of ammunition storage and shipping. Since 1942, the depot's mission has increased to include overhauling, rebuilding, and testing of wheeled and tracked vehicles; issue and shipment of chemicals and petroleum; and maintenance, demilitarization, and modification of ammunition. Several of these activities involve the use of TCE, other solvents, lubricants, corrosives, and various metals. LEAD is the owner/operator of two industrial

wastewater treatment plant (IWPT) lagoons. Sludge and waste material has leaked from the bottom of these lagoons into the underground water aquifer resulting in contamination of the groundwater. The two most significant VOCs identified in groundwater near the IWTP lagoons are TCE and trans-1,2-dichloroethylene. In order to remediate the groundwater at the IWPT lagoons, a water treatment plant was built which utilized air stripping followed by carbon adsorption.

Figure 2 is a process flow sheet of the LEAD system. The facility consists of two four foot diameter by 20 feet high towers made of fiberglass-reinforced plastic and filled with 3.5 inch Jaeger tri-pack poly packing. The two towers are operated in series. Contaminated water is pumped to the treatment site where the water is filtered through three 50 micrometer bag filters operated at 150 pounds/square inch (lb/in²) to remove suspended solids and preclude fouling of the tower packing or blinding of the final adsorber. A 2,000 gal polyethylene equalization tank was installed for blending the groundwater prior to air stripping. This tank serves as a holding tank set up to prevent the recovery wells from being pumped dry. As water leaves the second air stripper it is further cleaned in a 10,000 pound liquid-phase granular carbon adsorber. The water is then discharged through a four inch line about 130 feet from the facility into a nearby creek. Separate blowers push 1,000 ft³/min of air through each tower. The design air:water mass ratio is 50:1. A 10,000 pound vapor-phase carbon adsorber treats the off-gas from the first tower. Both carbon adsorbers were installed at the request of the Pennsylvania Department of Environmental Resources (PADER). A heated metal building encloses the entire water treatment facility.

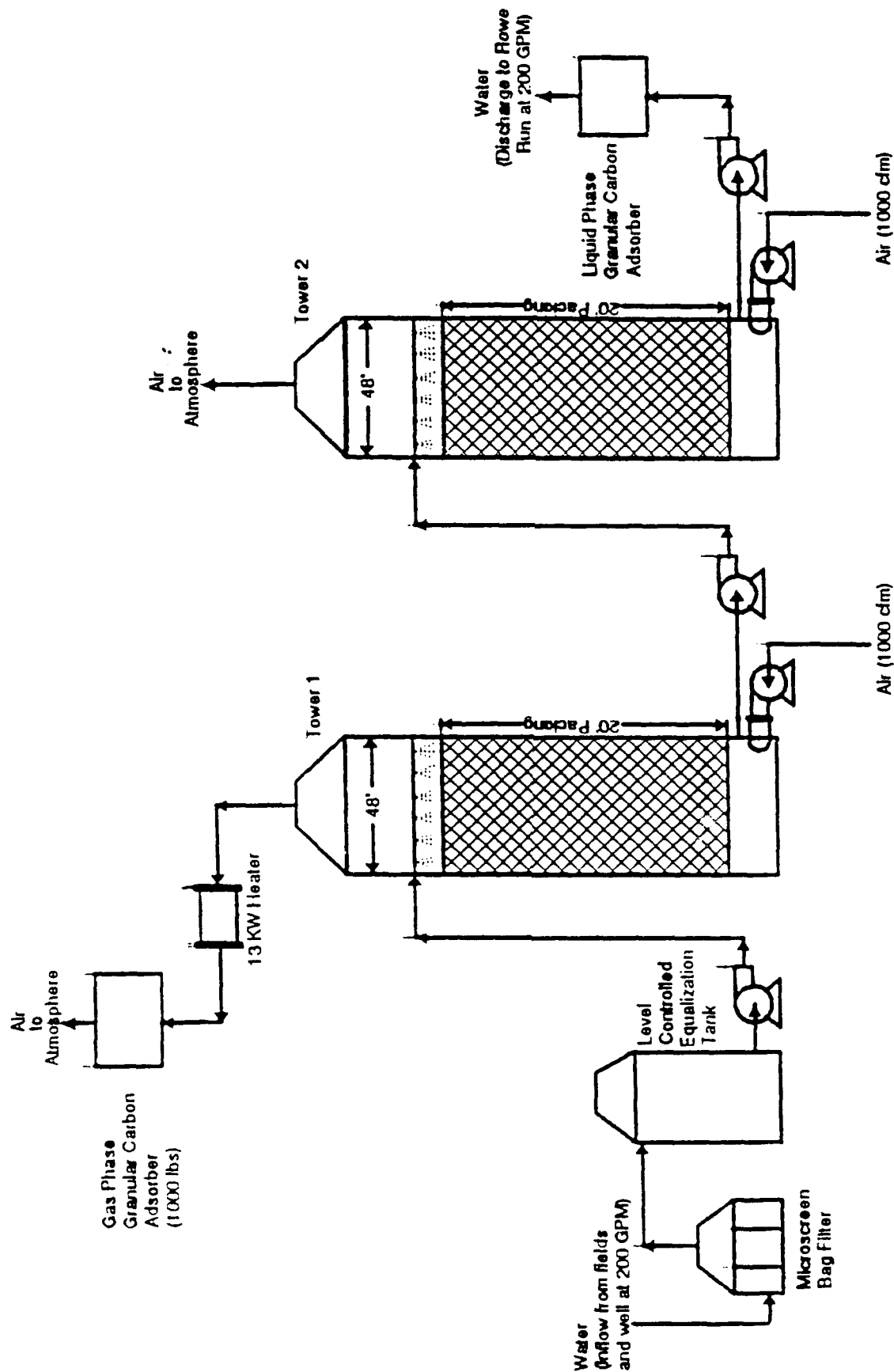
Ten recovery wells provide 200 gal/min of groundwater to the treatment facility. Schedule 80 PVC piping was laid directly from each well to the facility in a 48 inch deep trench.

While the plant is basically automated, an operator does remain on site to collect day to day readings and insure smooth operation of the facility.

SHAD

SHAD provided maintenance services for vehicles, aircraft, and industrial and medical equipment from 1941 to 1975. Organic solvents were used in these operations for degreasing, paint stripping, and paint spraying. Spent solvents and sludge from these operations were land applied. A 1981 environmental survey of SHAD determined that the contamination levels of TCE and its breakdown products in groundwater exiting the depot exceeded acceptable criteria. In order to reduce the VOC concentration in the groundwater, two packed-column air stripping water treatment plants have been constructed at SHAD and a third is planned.





Flowsheet of Water Treatment Plant at Letterkenny Army Depot

FIGURE 2

The two systems operating at SHAD are very similar in both design and operation. The data reported herein is based on the system located in the "North Balloon" area of the depot. Figure 3 shows is a flow diagram of the system. The basic air stripping system consists of two five foot diameter towers packed with approximately 9.25 feet of Cascade No. 1-A plastic 1 inch mini rings. The columns operate in series and process 300 gal/min of groundwater. One blower pushes air through both towers, in series, at a rate of 3,000 ft³/min. The air enters the bottom of the first tower, passes through the tower and is ducted to the bottom of the second tower. The air is then exhausted to the atmosphere from the second tower. The design air:mass ratio is 75:1. A significant difference in this plant design compared with the TCAAP and LEAD is the absence of a heated building and pumphouses. The mild climate at SHAD precludes the need for such precautions. (Plans are being prepared to add a vapor-phase carbon adsorption system to the exhaust stream. However, this modification is not included in this evaluation.) Groundwater treated in the air stripping system is sold off depot.

Fifteen boundary wells supply groundwater to the treatment facility. PVC piping is used for the forcemain system, some being laid in underground trenches.

The system currently operates continuously in an automatic mode. Maintenance is performed weekly to insure proper operation.

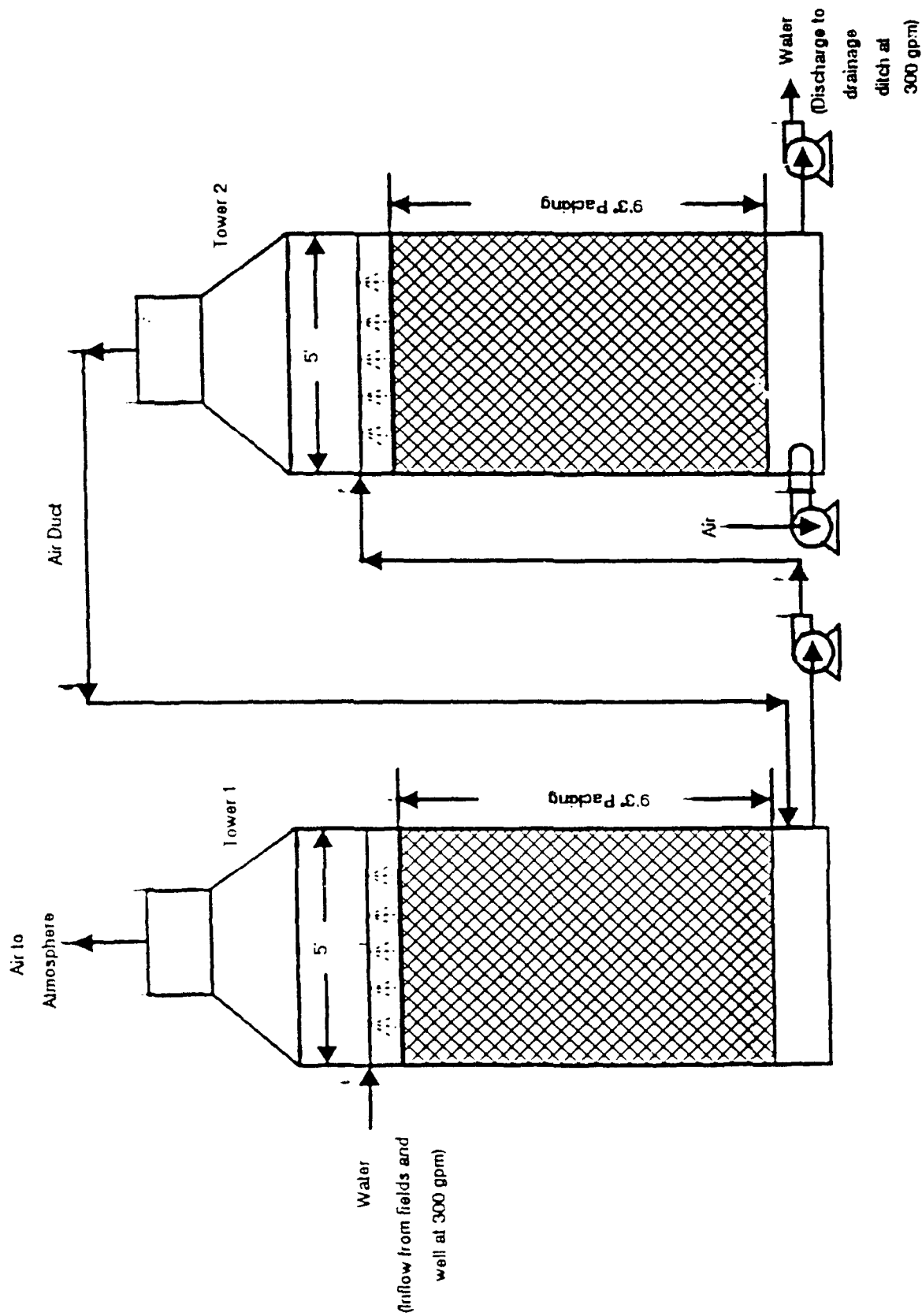
Economic Evaluation

The purpose of this study was to collect actual cost data where possible and determine what air stripping is costing the Government. In addition an attempt has been made to determine what major factors influence the costs associated with the procurement and operation of an air stripping facility.

This economic evaluation includes the following: capital cost of each facility, operating and maintenance cost of each facility, and total life-cycle costs for each facility expressed in dollars per 1,000 gallons of water treated. All costs were collected from actual data whenever available and put into constant 1990 dollars. The life of a plant was assumed to be 30 years.

Table 1 lists the capital and annual operational and maintenance costs for each facility studied. A comparison between the figures in Table 1 and the site descriptions lead to the identification of several major factors influencing the cost of operating an air stripping facility.

Perhaps the most obvious factor is facility size or capacity. TCAAP groundwater treatment plant processes 2,900 gal/min as compared to LEAD and SHAD which process 200-300 gal/min. The has almost doubled the cost of the treatment plant as compared



Flowsheet of Water Treatment Plant at Sharp Army Depot

FIGURE 3

TABLE 1

Capital and O&M Costs for Each Facility Studied

	<u>TCAAP</u>	<u>LEAD</u>	<u>SHAD</u>
<u>Capital Costs</u>			
Treatment Plant	1,937,693	1,050,938	458,871
Wells ¹	2,264,165	1,003,207	678,788
Forcemain System	3,832,596	²	245,504
<u>Annual Operating Costs</u>			
Utilities	148,846	23,827	9,687
Professional Services	244,677	7,621	
Maintenance	189,572	58,230	65,232
Carbon		132,400 ³	
<u>Tower Packing</u> (every 5 th year)	20,865	5,936	2,096

1 - TCAAP = 81 wells
 LEAD = 14 wells
 SHAD = 15 wells

2 - included in treatment plant costs

3 - Revised estimate = \$364,000

to LEAD, with TCAAP having two, two column trains and LEAD having only one. This effect on facility cost was also reported in a sensitivity analysis of the economic analysis for a third air stripping system proposed for SHAD. A second aspect of facility size is the geographic area covered by the groundwater collection system. Again TCAAP has a water recovery and monitoring system that is much larger than the other two facilities; 81 wells versus 14-15 wells at LEAD and SHAD. The wells are also spread out over a much larger area requiring an extensive forcemain system to bring the groundwater to the treatment facility. TCAAP laid 17,800 feet of 6-16 inch ductile iron piping whereas SHAD laid only 3,880 feet of 1-6 inch PVC piping and LEAD had only 400 feet of 1 inch PVC piping. These difference are reflected in the difference in capital costs between TCAAP and LEAD/SHAD.

A second factor that has influenced both the capital and operating costs of the facilities is geographic location and climate. Both TCAAP and LEAD require freeze protection whereas SHAD is in a more mild climate and requires no special protection from the elements. This requirement led to the construction of heated buildings to enclose the air stripping towers at both TCAAP and LEAD and to the construction of pumphouses on all wells at TCAAP. These requirements are reflected in both the capital costs for treatment plants and forcemain systems as well as the operating cost for utilities.

Operating requirement or philosophy is a third factor that has effected costs. This is easiest to see if LEAD and SHAD are compared. These plants are very similar in design and treatment capacity. However the SHAD facility is a relatively simple system that brings raw groundwater directly to the air stripping columns, passes the water through the columns, and releases the treated water. LEAD on the other hand requires a bag filter pretreatment of the groundwater to remove suspended solids; a 2,000 gal holding tank to allow intermittent operation of the well pumps so that the wells will not be pumped dry; and most significantly, both vapor- and liquid-phase carbon adsorbers to treat the off gas stream from the first air stripping tower and to polish the clean water effluent. These items all increased the capital cost of the treatment plant somewhat, however the main impact is the operating cost incurred for the carbon adsorbers. Carbon replacement represents approximately 59% of the annual operating cost in the original estimates. However after the system was in operation for some time the replacement rate had to be increased from every 90 days to every 25 days. This has increased the operating cost attributed to carbon replacement to the point where it is now 80% of the annual operating cost.

The last factor discussed here is harder to see directly from the data presented, the effect of design requirements versus available off-the-shelf components. The three sites studied all purchased available equipment. During the initial phases of

this study it was noticed that all the existing equipment was over designed for the performance required. It was later determined that the cause of this over design was the use of available components instead of components built to size. For example, at LEAD the design called for a 25 foot packed tower. However, the vendor already on contract had only 20 foot towers so two 20 foot towers were used in series. In general it is less expensive to purchase an off-the-shelf item over a specially fabricated one. However this may also increase the capital cost of the treatment plant over original production estimates.

Summary

The data collected for this study reflects the actual cost of fabricating and operating three separate underground water air stripping treatment facilities owned by the U.S. Army. When stripped to the basic components for an air stripping site, the costs reported appear to be equitable when compared between the three facilities. Some differences are possible simply because of variations in contractors and procurement practices at the different sites. However, the striking differences appear to be caused by facility size, geographic location or climate, and operating requirements.

Table 2 is a summary of the total life-cycle cost for each facility.

TABLE 2

Total Life-Cycle Cost per 1000 gal Treated

	<u>Gal/Min</u>	<u>TLCC</u>	<u>TLCC, \$/1,000 gal</u>
TCAAP	2,900	\$13,586,460	\$0.30
LEAD	200	\$ 4,162,427	\$1.32
SHAD	300	\$ 2,101,297	\$0.44



OFFSITE REMEDIATION OF CONTAMINATED ALLUVIAL GROUNDWATER AT ROCKY MOUNTAIN ARSENAL: PILOT-SCALE HYDRAULIC TESTING RESULTS APPLIED TO FULL-SCALE DESIGN

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ABSTRACT

A groundwater cleanup program was designed to remediate contamination of alluvial groundwater in the offpost operable unit of the Rocky Mountain Arsenal (RMA) National Priorities List (NPL) site in Commerce City, Colorado. The program is an interim response action (IRA) being performed in advance of the Record of Decision (ROD), as required by the terms of the Comprehensive Environmental Response, Compensation and Liabilities Act (CERCLA) as amended by the Superfund Amendments and Reauthorization Act (SARA) and the Federal Facility Agreement (FFA) for RMA. The IRA was designed and will be implemented under an accelerated schedule in order to minimize the future risk of exposure to contaminated groundwater and begin mitigation of alluvial groundwater contamination as soon as practicable. This IRA included assessing several potential remedial alternatives, and selecting and designing a cost-effective alternative that could be implemented in advance of the ROD. The design of the selected alternative included the use of groundwater extraction and recharge facilities (wells and trenches) placed either transverse or parallel to the axes of groundwater contaminant plumes, depending on plume characteristics. The water treatment facility designed for the IRA has a maximum design capacity of more than 44 liters per second. The final design was based upon the results of focused field investigations and pilot-scale testing in the target cleanup area. The field investigations included the use of surface and borehole geophysical tech-

niques, and hydrogeologic and hydrochemical data collection. Pilot-scale testing included the combined use of groundwater extraction and recharge tests, recharging water treated with a mobile water treatment facility. Review of the final IRA system design by the U.S. Army Corps of Engineers (COE) and parties to the FFA is complete. Construction of the system is scheduled to begin in November 1991, under the direction of COE.

INTRODUCTION

Remediation of environmental contamination is being undertaken at numerous U.S. Department of the Army (Army) facilities throughout the country. At Rocky Mountain Arsenal (RMA) near Denver, Colorado (Figure 1), environmental restoration programs have progressed through the remedial investigation (RI) stage, and the feasibility study (FS) process is ongoing. As a result of the RI process, two facts became apparent that led to the present study. First, contamination had extended beyond the RMA boundary onto private and municipal properties, and second, contamination was sufficiently severe at some RMA locations (both onpost and offpost) that remediation was advisable in advance of the selection and implementation of the final site remedy. The Army therefore initiated an Interim Response Action (IRA) process at RMA whereby these locations could be addressed in advance of the final remedy. This paper focuses on the hydraulic portions of the IRA undertaken to remediate alluvial groundwater contamination in the offpost area, just north of the RMA north bound-



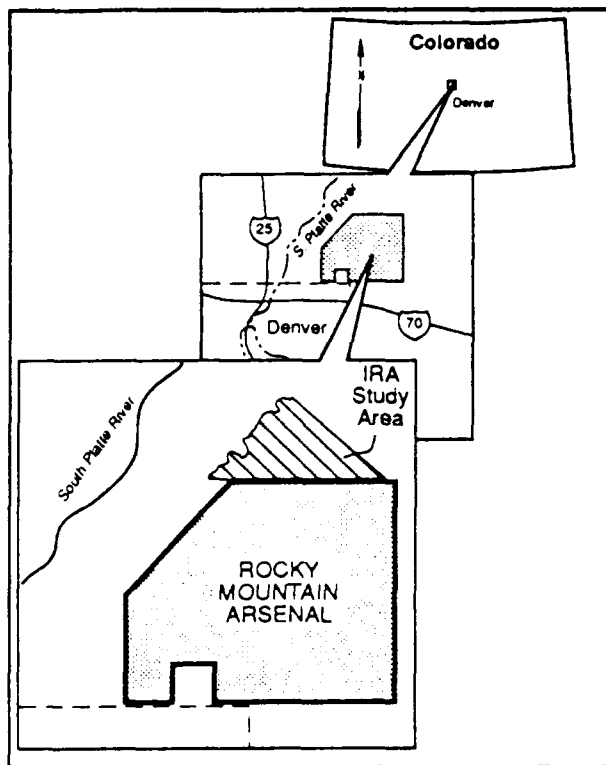


Figure 1. IRA STUDY AREA

ary (Figure 1). The specific objectives of this paper are listed below.

1. Describe the special technical, logistical, political, and public relations issues specific to working in the offpost area, on land not owned by the government.
2. Describe the data collected during field investigations to identify the locations for remediation and the methods that were used to select the locations.
3. Identify hydraulic components of the remedial design and the basis for their selection.
4. Describe the ways in which pilot-scale hydraulic testing data were used to scale up to full-scale design.
5. Describe the schedule for implementation of the remedial design.

Background

Rocky Mountain Arsenal (RMA) is located in Commerce City, Colorado, approximately 16 kilometers (km) northeast of Denver. Contamination of groundwater has occurred as a result of industrial and waste disposal practices of the Army and lessees associated with chemical and munitions

manufacturing and demilitarization at the site between the 1940s and the early 1980s.

The RMA site is on the National Priorities List (NPL) and is therefore being investigated and remediated under the regulatory auspices of CERCLA as amended by SARA. The site clean-up, schedules for implementation, and parties to the investigation are described in the Federal Facility Agreement ([FFA], 1989) for the site.

The RMA NPL site is subdivided into two operable units (OUs): the onpost OU and the offpost OU. The IRA described here was undertaken within the offpost OU. The IRA consists of the design and construction of an alluvial groundwater intercept and treatment system within the IRA study area (Figure 1). The delineation of the IRA study area is based on the results of the RI (ESE and others, 1988) that have shown:

1. The two primary pathways for offpost migration of contaminants in groundwater north of the RMA boundary are referred to as the First Creek and northern pathways. The pathways exist largely as a result of two paleochannels that were incised into the upper surface of the Denver Formation bedrock and were later filled with thick alluvial deposits. Migration of groundwater contaminant plumes in the IRA study area is generally limited to these two pathways. The plumes include various organic compounds that are the focus of the remedial efforts (Figure 2).
2. During investigations of groundwater contamination at RMA to date, the highest concentrations of contaminants have been shown to occur in the unconsolidated surficial geologic deposits beneath RMA, collectively known as alluvium. The highest concentrations of contaminants in the offpost OU occur in alluvial groundwater in the First Creek and northern pathways upgradient (south and southeast) of O'Brien Canal.

Groundwater in alluvial sediments within the study area is characterized by unconfined flow conditions and a north to northwest flow direction. The water table in some areas falls below the base of the alluvium into the underlying Denver Formation bedrock. Areas of unsaturated alluvium appear to exert some control over groundwater flow and associated contaminant migration, as is shown by the absence of groundwater contaminant plumes in areas of unsaturated alluvium (Figure 2).

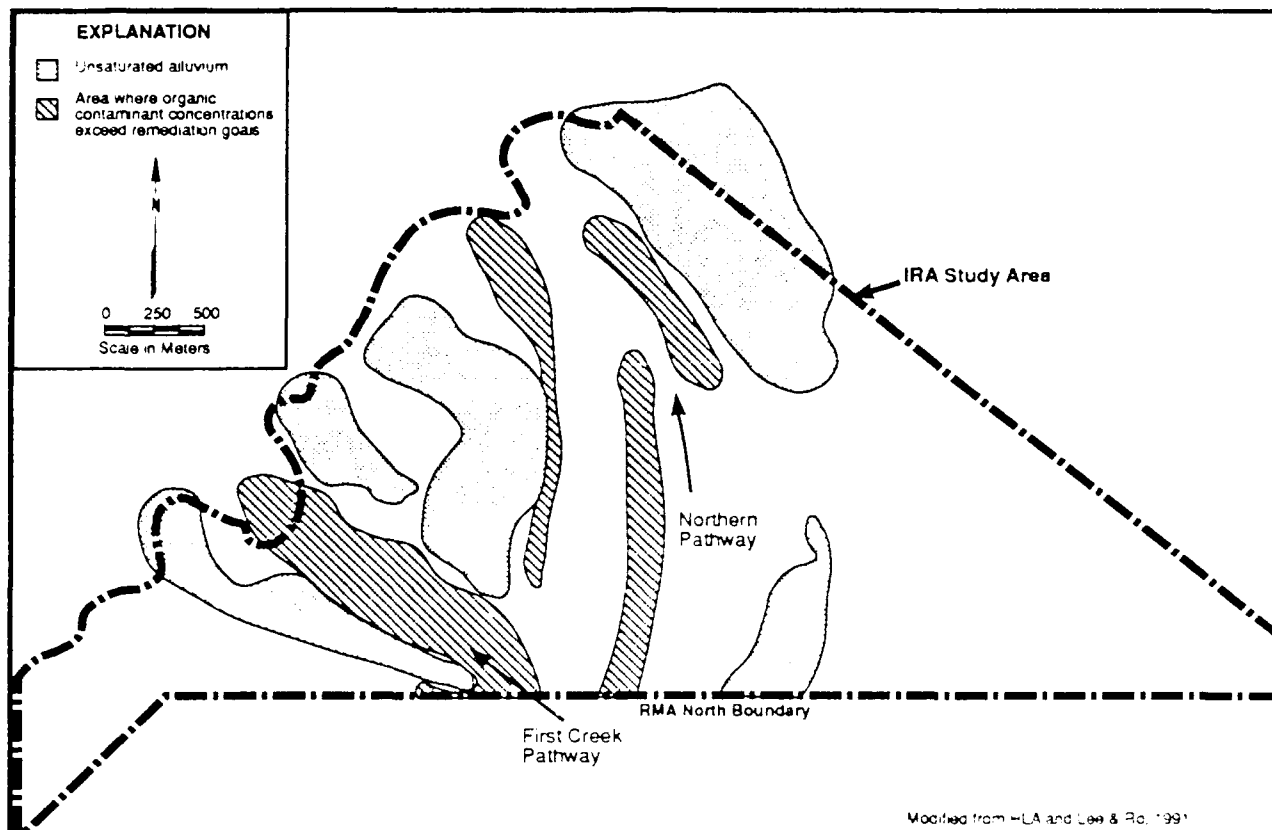


Figure 2. DISTRIBUTION OF CHEMICAL PLUMES WITHIN THE STUDY AREA

Interim Response Action Objectives

The overall objective of the IRA in the offpost OU is to reduce the risk of exposure to contaminated groundwater north of RMA (Ebasco and others, 1987). Although businesses and residents are not currently exposed to contaminated groundwater in the offpost IRA study area (ESE, 1988), the mitigation of contaminant migration is included in the offpost IRA to reduce the potential for future exposure and to begin aquifer remediation in advance of the final remedy. The specific objectives of the IRA are listed below.

1. Mitigate migration of contaminants in alluvial groundwater as soon as practicable.
2. Treat contaminated alluvial groundwater to provide a beneficial impact on groundwater quality.

Interim Response Action Alternatives

Alternatives to implement the offpost IRA were investigated through a comparison of the remediation requirements, technologies that were readily available (and could thus be implemented without the need for treatability studies), the effectiveness

of the technologies, and the institutional, environmental, and cost impacts of each technology (HLA, 1989). As a result of the investigative process, two potential groundwater extraction and recharge technologies, wells and subsurface drains (trenches), were identified as potentially useful for the IRA. The process also included consideration of several methods for treatment of organic contaminants in groundwater. As a result, two potentially useful treatment technologies were identified from a list of eight that were considered. These two technologies were treatment by granular activated carbon (GAC) alone and treatment by GAC with air stripping as a pretreatment step. The focus of this paper is the hydraulic components of the IRA design; the treatment design process will not be discussed further, but will be presented in a subsequent paper.

CONSIDERATIONS WHEN WORKING IN THE OFFPOST AREA

All work conducted during the IRA was performed within the offpost OU on land owned by either private citizens or nearby municipalities. As a result, the work generated significant interest on the part

of private citizens, citizen groups, local and regional regulatory agencies, and the media. During the program, significant effort was directed toward regularly providing information to these groups and to obtaining access to these properties. Work involved in obtaining access included identification of owners of record, preparation of access agreements, and numerous presentations to the various landowners. Public meetings were held to inform the public of the ongoing IRA efforts and to elicit community involvement.

In addition to the considerations noted above, special technical and logistical problems had to be addressed while working offpost. These included the need to transport waste materials generated during field investigations across public roadways, the lack of security in the study area, the need to access land that was being used for purposes that would be intruded upon by field work (i.e., crop cultivation), and the lack of utilities (i.e., water, power, sanitary sewer) to support field investigations.

FIELD INVESTIGATIONS

Field investigations were conducted to obtain the information that, in conjunction with information obtained during the RI, would provide the detail necessary to (1) locate the IRA facilities, (2) select components of the remedial design, and (3) support full-scale design of extraction and recharge facilities in the First Creek and northern pathways. The field investigations included a geologic investigation, a groundwater monitoring program, and pilot-scale testing.

Geologic Investigation

The geologic investigation consisted of a geophysical program and a drilling program. The investigation focused on the alluvial system and was specifically designed to assess paleochannel configurations, including width and depth to competent Denver Formation bedrock and geologic variability of alluvium within each pathway. In addition to supporting full-scale design, results of these studies were also used to select sites for pilot-scale testing.

The geophysical program was conducted to assist in finalizing drilling locations and to aid in assessing paleochannel configurations. To meet these objectives, three geophysical techniques were employed: borehole induction logging, soil conductivity profiling, and vertical electrical soundings.

Borehole induction logging provided an assessment of the vertical variability in electrical conduc-

tivity between alluvium and the underlying Denver Formation, and thereby provided an indication of the usefulness of soil conductivity profiling.

Monitoring wells were logged using a Geonics EM39 induction logging tool. Results of this work indicated that the conductivity of the Denver Formation is two to three times greater than the conductivity of alluvium. Therefore, soil conductivity profiling was considered a viable technique for accomplishing the objectives of the geologic investigation.

Soil conductivity profiling was performed using a Geonics EM34-3 inductive conductivity measuring system. Four linear electromagnetic (EM) profiles, ranging in length from approximately 1.7 km to 3.4 km, were performed.

Vertical electrical soundings (VESs) were performed in areas where (1) anomalous readings were obtained during EM profiling or (2) cultural features rendered EM profiling ineffective. VES data were combined with EM data to complete the EM profiles.

The drilling program included drilling 47 soil borings and installing seven alluvial monitoring wells. The drilling program was conducted to assess paleochannel configurations, the character and distribution of alluvial lithologic units, and the distribution of unsaturated alluvium. A lithologic log was prepared for each completed boring and monitoring well.

Groundwater Monitoring Program

The groundwater monitoring program included collecting groundwater samples for chemical analysis and obtaining water-level measurements from each new alluvial monitoring well. Water-quality monitoring was performed to augment historical data and to assess the distribution of organic contaminants within the alluvium in each pathway.

The monitoring data were also used to estimate expected influent chemical concentrations in the areas anticipated for pilot-scale testing. The analytical data were a crucial element in the selection of final remediation system hydraulic components.

Pilot-Scale Testing

Pilot-scale testing was performed in both pathways to collect sufficient aquifer hydraulic system data to support full-scale design of groundwater extraction and recharge facilities in both the First Creek and northern pathways. Testing was performed in each pathway at sites selected on the basis of geologic



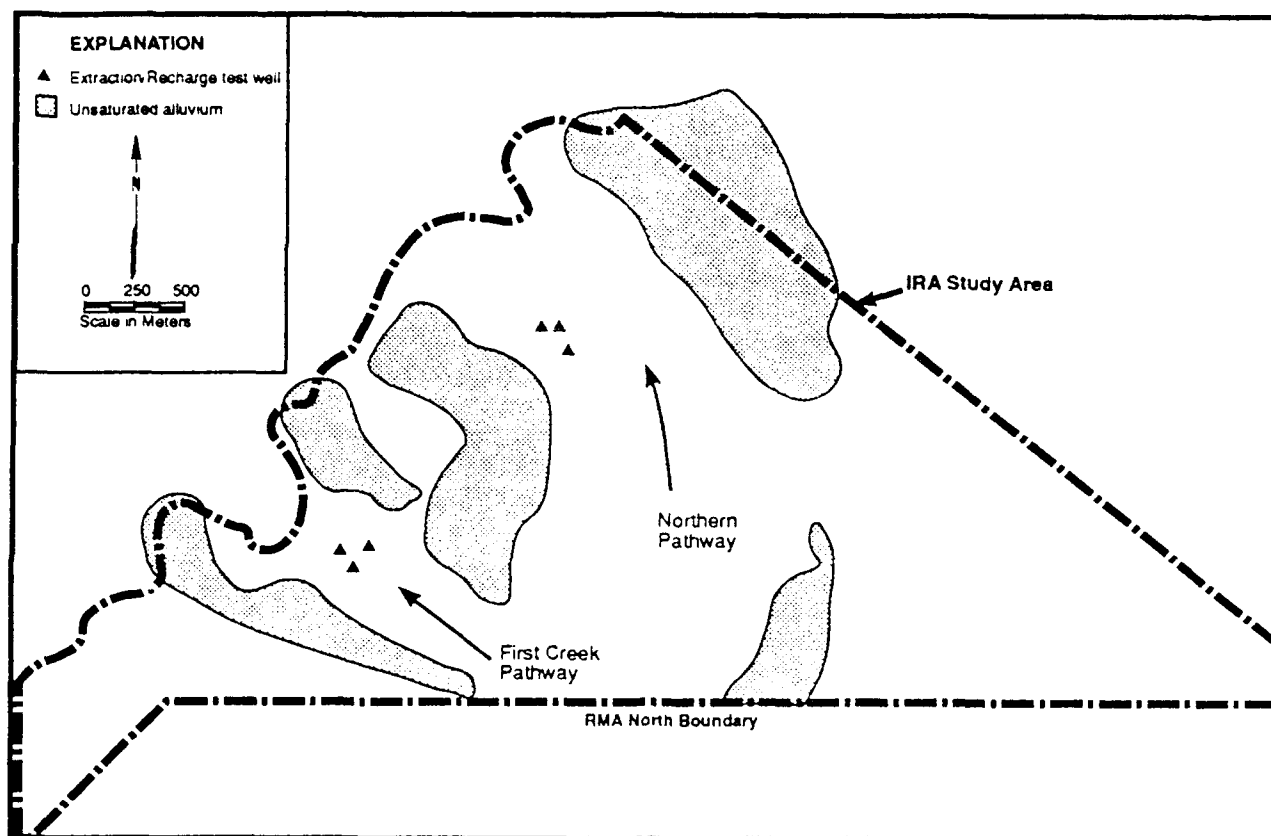


Figure 3. TEST WELL LOCATIONS FOR PILOT - SCALE TESTING

investigation results with the goal of testing the range of probable geologic conditions that were likely to be encountered during construction of the final IRA system.

Pilot-scale testing was conducted in two phases. Phase I consisted of individual aquifer tests at each of six test wells (Figure 3). The goal of this phase of testing was to obtain hydraulic data that could be used to estimate aquifer characteristics for design purposes. Testing at each well consisted of (1) a step-drawdown test, (2) a recovery period, (3) a 24-hour constant-rate pumping test, and (4) recovery monitoring.

Phase II hydraulic testing included four-day extraction/recharge tests conducted in each of the two pathways to evaluate the recharge capacity, including the potential for well clogging, of selected test wells. Testing in each pathway consisted of (1) pumping water from one test well (extraction well), (2) treating the extracted groundwater using a pilot-scale mobile GAC treatment unit, and (3) recharging treated effluent into the alluvial aquifer at two wells (recharge wells) for approximately 96 hours.

APPLICATION OF FIELD INVESTIGATION RESULTS TO FULL-SCALE DESIGN

Results of the field investigation were evaluated in conjunction with interpretations made during the RI (ESE and others, 1988) to assess (1) the locations of areas requiring remediation, (2) hydraulic system components, (3) hydraulic system configurations, and (4) design flow rates.

Locations of Areas Requiring Remediation

The locations of the areas requiring remediation were assessed on the basis of analytical results for groundwater samples collected from alluvial monitoring wells. Analytical results obtained during the IRA field investigation as well as during concurrent RMA groundwater monitoring programs indicated that chemicals are present at concentrations above remediation goals in alluvial groundwater within each of the two pathways. In addition, the results indicated that chemical concentrations are generally higher in the First Creek pathway than in the northern pathway.

Within the First Creek pathway, a continuous plume of contaminated groundwater with chemi-

cals at concentrations above remediation goals was interpreted to extend from RMA to just beyond the study area boundary (Figure 2). The highest concentrations within the pathway were reported in samples from wells located near the northernmost extent of the First Creek pathway, near the study area boundary. On the basis of these results and the fact that access could not be obtained outside the study area within the schedule established for implementation of the IRA, the area of highest chemical concentrations within the IRA study area was selected as the preferred location for groundwater remediation.

Within the northern pathway, discontinuous plumes of organic contaminants were identified between RMA and the study area boundary (Figure 2). None of the plumes were interpreted to extend outside the study area. Because chemicals at concentrations above remediation goals were detected in a few wells located near the study area boundary, the area adjacent to the boundary was selected as the preferred location for groundwater remediation in the northern pathway.

Selection of Hydraulic System Components

The hydraulic system components considered for groundwater extraction were wells and subsurface drains. Groundwater extraction using wells was tested successfully during pilot-scale testing in both pathways at extraction rates above the rates expected during full-scale operation. Hydraulic data collected during aquifer testing indicated that the alluvial aquifer transmissivity was sufficiently high that groundwater extraction using wells would be an effective long-term alternative to subsurface drains. In addition, extraction wells have successfully been used at the three groundwater intercept and treatment systems currently operating at RMA. As a result of these factors, and because wells are less costly and easier to construct and maintain than subsurface drains, wells were selected as the preferred alternative for groundwater extraction in both the First Creek and northern pathways.

The hydraulic system components considered for recharge of treated water were wells and recharge trenches. Pilot-scale tests were conducted to qualitatively assess the ability of the alluvial aquifer to accept recharge water. Of particular interest was the ability of the aquifer to accept recharge rates comparable to extraction rates experienced during Phase I aquifer tests, and the potential for clogging of recharge wells. In addition to pilot-scale test results, other advantages and disadvantages of us-

ing wells or trenches were considered in the selection of recharge components for the IRA. The advantages of using wells include ease of installation, lower capital cost, lower volume of waste generated during construction, the relative ease with which a target recharge zone can be accessed, and the ability to rehabilitate wells. In contrast, recharge trenches cannot be rehabilitated, they generate large volumes of waste materials during construction, and they have a high capital cost, but low operation and maintenance cost. The primary advantages of recharge trenches, then, is that (1) they are most effective in spreading recharge over a large area, thereby increasing lateral head buildup in the aquifer but reducing vertical increases in hydraulic head, and (2) they may intercept multiple recharge zones in heterogeneous aquifers, such as those characterized by lenticular sands interspersed with clays and silts.

Within the First Creek pathway, recharge trenches were selected as the preferred recharge alternative. In this pathway, shallow water table conditions (1 to 2 meters below ground surface) limited the available vertical head buildup during pilot-scale recharge testing. Although recharge tests during pilot-scale testing showed that recharge using wells is possible, resulting recharge rates were below those expected during full-scale operation because of the shallow water table and limited allowable head buildup. However, sufficient recharge rates using trenches could be achieved because of the ability of trenches to allow distribution of recharge over a wide area and therefore to limit relative head buildup for a given recharge rate. In addition, the recharge potential of geologic materials was similar throughout the alluvial section because of the homogeneity of the sediments. Recharge trenches have proven to be highly successful at an existing RMA groundwater recharge site located near the offpost OU with geologic and hydrologic characteristics similar to those within the First Creek pathway. Clogging of recharge wells was not observed during pilot-scale testing, indicating that frequent rehabilitation of recharge facilities would not be needed; thus the inability to rehabilitate the trenches was not considered a serious threat to their operation for the IRA.

Within the northern pathway, wells were selected as the preferred recharge alternative. Recharge wells were selected because excessive head buildup is not expected to be a problem in the northern pathway because the depth to water (greater than 6 meters) is significant, allowing a



large vertical zone for potential head buildup without causing marshy conditions at the surface. Another reason wells were selected for northern pathway recharge was that the aquifer is overlaid by as much as 6 meters of silty sand, silt, and clay. The target recharge zone is located at the base of the aquifer, at a depth of approximately 11 to 13 meters. Therefore, the recharge trench depth that would be required to reach the target recharge zone makes recharge wells more economical in the northern pathway.

Hydraulic System Configurations

The configurations of extraction/recharge wells and recharge trenches were designed to provide the most beneficial impact on the alluvial aquifer within the areas selected for groundwater remediation in each pathway. The configurations considered included placing extraction/recharge facilities either across the pathway, referred to as a transverse system, or along the pathway axis, referred to as an axial system. Transverse systems are generally designed to provide capture of groundwater flowing through the pathway, while axial systems are generally used to allow the most rapid removal of chemical mass, but do not generally provide a complete hydraulic barrier to downgradient migration of contaminants in groundwater.

An axial system was selected as the preferred configuration within the First Creek pathway because chemical plumes may extend beyond the area selected for groundwater remediation; therefore, a transverse system would not provide capture of contaminants that have already bypassed the study area boundary. In addition, the area selected for groundwater remediation contains the highest concentrations of chemicals present within the pathway. The enhanced flushing of contaminants toward the system afforded by the axial system would allow more rapid removal of contaminant mass, and an associated reduction in required remediation time. Although it is not possible to demonstrate complete capture using an axial system, wells and trenches were placed to minimize the potential for contaminated groundwater to bypass the extraction system.

A transverse system was selected as the preferred configuration within the northern pathway. The system will be placed near the study area boundary, downgradient of the interpreted extent of chemical concentrations above remediation goals. The system is designed to provide containment of chemical plumes approaching the system. In addition, the

concentrations of contaminants were sufficiently low that enhanced flushing of the system using axial wells would not appreciably reduce the anticipated operational life of the system.

Data obtained during pilot-scale testing were evaluated analytically to evaluate the optimum number, location, and spacing of wells and trenches for the full-scale extraction/recharge system in each pathway. Numerous well and/or trench arrays were evaluated, and the most appropriate array was selected to maximize either plume capture or chemical mass removal. As a result of these analyses, an array of 12 extraction wells and 24 recharge wells was selected in the northern pathway, while the hydraulic system in the First Creek pathway consists of five extraction wells and six recharge trenches (Figure 4).

Design Flow Rates

Results of pilot-scale testing were also used to estimate groundwater flow rates through each pathway as well as the pumping and recharge rates required to achieve IRA remediation objectives. Groundwater flow rates through the pathways were estimated using the results of pilot-scale hydraulic tests in each pathway and considering the impact of recycling water during groundwater extraction and recharge while using the well and/or trench arrays selected within each pathway. Groundwater extraction and recharge rates of 11.4 and 18.9 liters per second were estimated for the First Creek and northern pathways, respectively. This information was used to establish sizes for water transport pumps and pipelines to and from a single IRA water treatment plant, and to determine the capacity of the plant.

IMPLEMENTATION SCHEDULE

Construction of the IRA groundwater intercept and treatment system is scheduled to begin in November 1991. The treatment plant and pipelines between the treatment plant and northern pathway extraction and recharge system will be constructed concurrently and will be completed within approximately 10 months. The northern pathway extraction and recharge system will be constructed following completion of the treatment plant and will be completed in approximately four months, allowing initial remediation to begin in early 1993. To effectively manage the high water table in the First Creek pathway, and associated construction dewatering that will be required, this system will be constructed during the first six months of treatment.

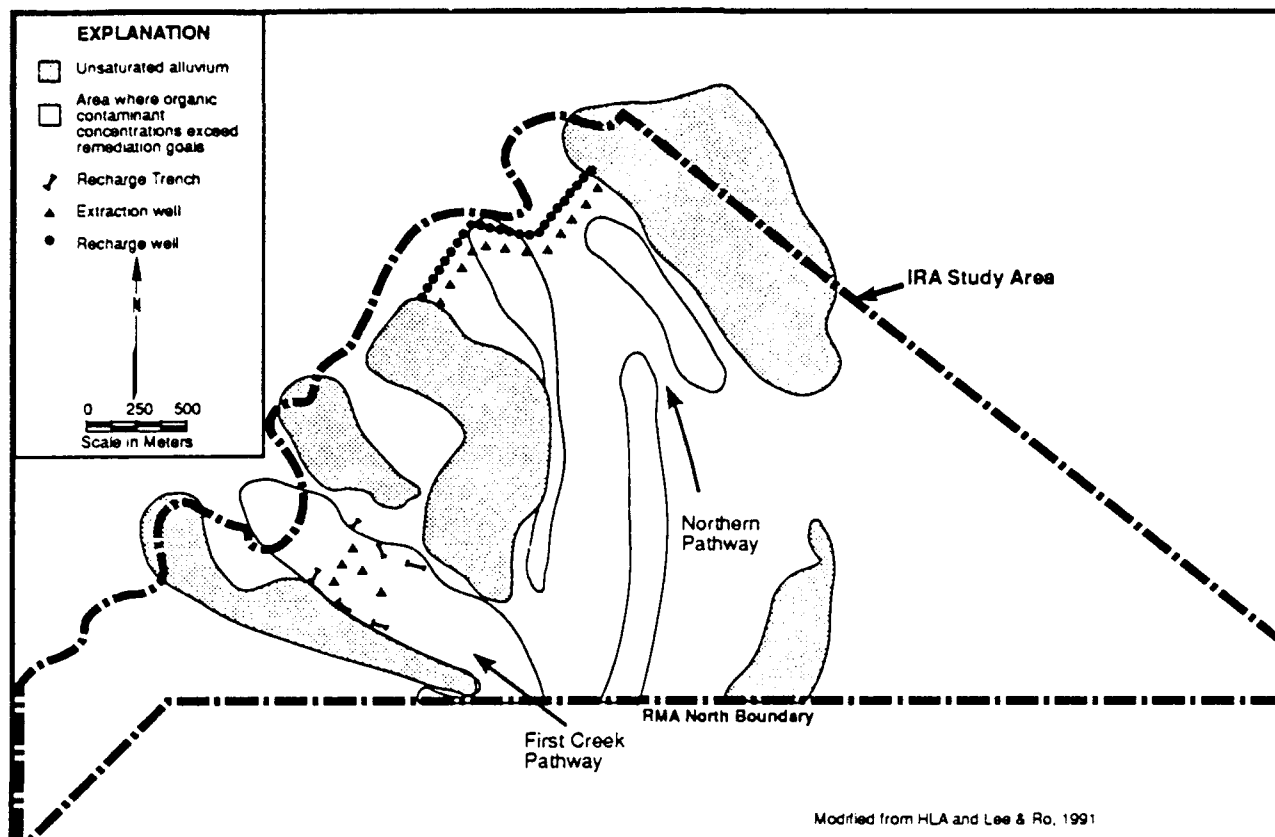


Figure 4. PROPOSED LOCATIONS FOR EXTRACTION AND RECHARGE FACILITIES

plant operation. Using this schedule will allow the treatment plant to treat contaminated groundwater generated during construction dewatering in the First Creek pathway, as well as groundwater from the northern pathway extraction wells. Before completion of the First Creek pathway system, all treated water will be recharged through northern pathway recharge wells. Operation of the full-scale intercept and treatment system is scheduled to begin in Summer 1993.

SUMMARY

An IRA has been designed and will soon be constructed to remediate alluvial groundwater contamination within the offpost OU, north of RMA. The IRA is intended to begin remediation of organic groundwater contamination that has migrated beyond the RMA northern boundary along two primary pathways, referred to as the First Creek and northern pathways. The IRA will consist of alluvial groundwater extraction from each pathway, treatment of extracted groundwater using GAC, and recharge of treated water to the alluvial aquifer within each pathway.

Special technical, logistical, political, and public relations issues had to be addressed as part of the design because the IRA will be located on land owned either by private parties or nearby municipalities. These issues included access for field investigations, handling and transport of waste materials generated during field efforts, public relations, and community involvement.

Field investigations, including geophysics, a drilling program, a water-quality monitoring program, and pilot-scale hydraulic testing, were performed in support of full-scale system design. Field investigation results were evaluated in conjunction with RI data to locate the IRA facilities, select components of the remedial design, and support full-scale design of extraction and recharge facilities.

The locations of IRA facilities were assessed on the basis of the distribution of contaminants in alluvial groundwater within each pathway. Within the First Creek pathway, extraction and recharge facilities will be aligned along the pathway axis to allow the most rapid removal of chemical mass from the area of highest chemical concentrations. Northern

pathway extraction and recharge facilities will be aligned across the pathway, beyond the interpreted extent of chemical concentrations above IRA remediation goals. The northern pathway configuration will provide containment of chemical plumes approaching the system.

Groundwater extraction will be performed using extraction wells in both pathways. Hydraulic data collected during aquifer testing indicated that alluvial aquifer transmissivities in both pathways were sufficiently high that wells would provide an effective long-term alternative for groundwater extraction.

Treated water will be recharged using recharge trenches in the First Creek pathway. Recharge trenches were selected because shallow water table conditions in this pathway limited the available buildup of hydraulic head during pilot-scale recharge testing. Recharge trenches will allow distribution of recharge over a wide area, and therefore, limit vertical head buildup.

Wells were selected as the preferred method to recharge treated groundwater in the northern pathway. Excessive head buildup is not expected to be a problem in the northern pathway because the depth to water is significant, allowing a large vertical zone for potential head buildup. In addition, the target recharge zone is located at the base of the aquifer within this pathway. Therefore, recharge wells were considered more effective and less costly than recharge trenches in directing recharge to the target recharge zone.

The most appropriate well and/or trench arrays were selected on the basis of pilot-scale testing results to maximize either plume capture or chemical mass removal. An array of 12 extraction wells and 24 recharge wells was designed in the northern pathway, while the hydraulic system in the First Creek pathway will consist of five extraction wells and six recharge trenches.

Construction of the IRA is scheduled to begin in November 1991. The construction sequence will include construction of the treatment plant followed by construction of the northern pathway system and the First Creek pathway system. This schedule will allow initial remediation to begin in early 1993, and full-scale operations to begin in Summer 1993.

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RISK ASSESSMENT OF MUNITIONS
CHEMICALS TO DEVELOP DRINKING
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The United States Department of Defense relies on numerous chemicals, many which are unique to or related primarily to military operations, to conduct activities necessary for defense and security. Military munitions activities (e.g., manufacture, production, transport, storage, demilitarization, and use) exemplify operations that produce wastes and environmental contamination. There is potential for the munitions chemicals to pollute ground and surface waters. U.S. military health and engineering professionals have identified many chemicals from defense operations that have public and environmental health concerns (Burrows et al., 1989; Rosenblatt et al., 1973; Uhrmacher et al., 1985; Small and Rosenblatt, 1974; Ryon et al., 1984; Kitchens et al., 1979). In 1985 the United States Environmental Protection (EPA) (Assistant Administrator for Water) and the United States Department of the Army (Deputy for Environment, Safety, and Occupational Health) established a Memorandum of Understanding to develop EPA Drinking Water Health Advisories (HAs) for Army environmental contaminants (MOU, 1991). The following presentation discusses the risk assessment methodology for drinking water HAs and presents advisory values derived by this method for Army environmental contaminants.

Health Advisories provide specific advice on the levels of contaminants in drinking water at which adverse health effects would not be anticipated and include a margin of safety to protect the most sensitive members of the population at risk (USEPA, 1989a). The HAs provide technical guidance to assist public health professionals when contaminations and spills occur. Publishing the advisories is discretionary under the authority of the Safe Drinking Water Act (SDWA) § 1442(b)(1). They are not legally enforceable standards, are not issued as official regulations, and do not condone the presence of a contaminant in drinking water. The HAs contain a summary of the relevant literature on chemical and physical properties, occurrence, environmental fate, pharmacokinetics, human and animal health effects, analytical methods, and treatment technologies (Table 1) (USEPA, 1989b). These data are used to calculate HA values for specific exposure durations. An addendum to each of the munitions HAs identifies deficiencies and problems in the toxicological literature, and recommends appropriate research to enhance the health effects database (MOU, 1991).

Health advisory values are based on systemic noncarcinogenic health



TABLE 1. DRINKING WATER HEALTH ADVISORY CONTENTS^a

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- o Introduction
 - o General Information and Properties
 - o Pharmacokinetics
 - o Health Effects
 - o Quantification of Toxicological Effects
 - o Other Criteria, Guidance and Standards
 - o Analytical Methods
 - o Treatment Technologies
 - o References
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^a/ Adapted from USEPA (1989b).

effects from animal or human studies (USEPA, 1989a). This method assumes that adverse systemic health effects occur when a biological threshold is exceeded. One- and Ten-Day HAs are developed to protect a 10 kg child who is assumed to consume 1 liter of water daily. Longer-term HAs are calculated for both the 10 kg child who is assumed to consume 1 liter and for a 70 kg adult who is assumed to consume 2 liters of water daily. A Lifetime HA and the cancer risk estimates are to protect a 70 kg adult who is assumed to consume 2 liters of water daily.

The highest dose at which there is no significant adverse effect (No-Observed-Adverse-Effect- Level, NOAEL) and the lowest dose at which there is a significant adverse effect (Lowest-Observed-Adverse-Effect- Level, LOAEL) are noted for each study. The advisory value is calculated from a NOAEL or LOAEL from the most sensitive toxic endpoint and from a test species that is toxicologically relevant to humans. Uncertainty factors (UF), adjustments for body weight (BW), and the rate of water consumption (in liters per day, L/day) are applied to the NOAEL or LOAEL. Uncertainty factors (usually a factor between 1 and 10) compensate for uncertainty that may arise from the quality and nature of the data. The basic formula for calculating less-than lifetime (i.e., one-day, ten-day, and longer-term) HA values (in milligrams per liter [mg/L] or micrograms per liter [µg/L]) is:

$$HA = \frac{(NOAEL \text{ or } LOAEL) (BW)}{(UF) (\text{L/day})} = \text{___ mg/L (or ___ } \mu\text{g/L)}$$

A lifetime HA is derived by a three step calculation: (1) determination of a reference dose (RfD); (2) determination of a drinking water equivalent level (DWEL); and (3) determination of the lifetime HA (USEPA, 1989b). The RfD is an estimate, with an uncertainty of perhaps an order of magnitude, of a daily exposure that is likely to be without appreciable risk of deleterious health effects

in the human population (including sensitive subgroups) over a lifetime. The DWEL represents the concentration of a substance in drinking water that is not expected to cause any adverse noncarcinogenic health effects in humans over a lifetime of exposure, assuming that all exposure comes from drinking water. The Lifetime HA reduces the DWEL in proportion to the amount of exposure from drinking water relative to other sources (e.g., food, air). In the absence of actual exposure data, this relative source contribution (RSC) generally is assumed to be 20%. If the chemical is classified as a possible human carcinogen (EPA Group C), an additional uncertainty factor may be applied to the lifetime HA to provide an additional margin of safety. The formulas for the three step calculation are:

$$\text{STEP 1.} \quad \text{RfD} = \frac{(\text{NOAEL or LOAEL})}{\text{UF}} = \text{ ______ } \text{ mg/kg bw/day}$$

$$\text{STEP 2.} \quad \text{DWEL} = \frac{(\text{RfD}) (70\text{kg})}{(2\text{L/day})} = \text{ ______ } \text{ mg/L (______ } \mu\text{g/L)}$$

$$\text{STEP 3.} \quad \text{Lifetime HA} = \text{DWEL} \times \text{RSC} = \text{ ______ } \text{ mg/L (______ } \mu\text{g/L)}$$

The EPA classifies contaminants according to their potential to produce cancer in humans (USEPA, 1986, 1989a). They are classified as either known, probable, or possible human carcinogens (Groups A, B, C, respectively). They also may be classified as Group D when there are inadequate or no experimental studies, or as Group E when there is evidence of no carcinogenicity in humans. Lifetime advisory values are not recommended for Group A or B; however, mathematical models are used to estimate the risk of developing cancer. The models estimate an upper-bound excess cancer risk for consuming contaminated water during a lifetime. There are several models that will estimate cancer risk; however, because the mechanism of cancer is not well understood, there is no evidence that any one model is more accurate than the others. The EPA has adopted the linearized multistage model (LMS) which is one of the more conservative models (USEPA, 1986). This model fits linear dose-response curves to low doses, and is consistent with a non-threshold model of carcinogenesis which assumes that every exposure to a carcinogen produces an increased cancer risk (NAS, 1986; USEPA, 1989a). The dose-response data is used to calculate a potency value (unit risk, potency factor, q_1^*) that can be used to determine the concentrations in drinking water that are associated with theoretical upper-bound excess lifetime cancer risks of 10^{-4} , 10^{-5} , and 10^{-6} (i.e., the possibility of 1 excess cancer per population of ten-thousand, one-hundred-thousand, or one-million, respectively) (USEPA, 1989a). The HAs also list the concentrations in drinking water that are associated with theoretical upper-bound excess lifetime cancer risks of 10^{-6} calculated by the probit, logit, one-hit, and

TABLE 2. MUNITIONS HEALTH ADVISORY VALUES

Chemical	Health Advisory Values (mg/L)					DWEL ^a (mg/L)	EPA Cancer Group ^b
	1- Day	10- Day	Longer-Term (Child): (Adult)		Life- Time		
Trinitroglycerol	0.005	0.005	0.005	0.005	0.005	na ^c	na
Nitrocellulose	--d	--d	--d	--d	--d	--d	na
RDX	0.10	0.10	0.10	0.40	0.002	0.10	C
HMX	5.00	5.00	5.00	20.00	0.40	2.00	D
Trinitrotoluene	0.02	0.02	0.02	0.02	0.002	0.02	C
DIMP	8.00	8.00	8.00	30.00	0.60	3.00	D
Nitroguanidine	11.00	11.00	11.00	37.00	0.74	4.00	D
1,3-Dinitrobenzene	0.04	0.04	0.04	0.14	0.001	0.005	C
White Phosphorus	--e	--e	--e	--e	0.0001	0.0005	D
Hexachloroethane	5.00	5.00	0.10	0.50	0.001	0.04	C

a/ Drinking water equivalent level; 100% contribution from water.

b/ C = possible human carcinogen; D = not classifiable as to human carcinogenicity.

c/ Not applicable.

d/ Not toxic.

e/ Values not recommended due to extreme toxicity.

Weibull models.

Table 2 displays the lifetime and shorter-term advisory values for the published HAs. The following is a discussion of the advisory values for each of the ten munitions chemicals, and includes the basis of the values, genotoxicity, and carcinogenicity. The order of discussion is chronological, by publishing date, and does not reflect toxicological significance or potency.

Trinitroglycerol

Trinitroglycerol (TNG), also known as glyceryl nitrate and nitroglycerin, is an aliphatic nitrate ester, and has been used as an explosive since 1864 (Sullivan et al., 1979a). Humans may be exposed to TNG clinically (as a vasodilator), occupationally, or as an environmental contaminant (Rosenblatt et al., 1973; Shiotsuka et al., 1979). The major health effects in acutely exposed people are: relaxation of smooth muscle, vasodilatation, hypotension, dizziness, fainting, headache, and rapid pulse rate. Chronic exposure has been associated with chest pain, ischemic heart disease, and the development of



tolerance. Death has occurred subsequent to both acute (from respiratory paralysis) and chronic (from myocardial infarction) exposures.

The HA value for TNG is 0.005 mg/L (5 µg/L) for all durations of exposure and for both adults and children (USEPA, 1987a). This HA is based upon the sublingual administration of TNG in the treatment of acute angina in humans. The therapeutic dose range is usually 0.15 to 0.60 mg which may cause a marked hypotensive effect and result in transient episodes of dizziness, weakness, and other manifestations of cerebral ischemia (Needleman and Johnson, 1980). Assuming the average weight of an adult is 70 kg, the usual dose ranges from 0.002 to 0.009 mg/kg, which has an arithmetic mean of 0.005 mg/kg. The one-day HA value, which is to protect a 10 kg child who is not known to consume 1 liter of water per day, is calculated to be 0.005 mg/kg day.

Trinitroglycerol's genotoxic and carcinogenic potential were considered and reviewed for the development of the HA. Mutagenic activity was either absent or weak in assays with bacteria (*Salmonella typhimurium*) and yeast (*Saccharomyces cerevisiae*) with and without metabolic activation (Ellis et al., 1978b; Simmon et al., 1977). Trinitroglycerol was not genotoxic or mutagenic in *in vitro* mammalian test systems to include rat bone marrow and kidney cell cultures, lymphocytes from dogs and rats, and Chinese Hamster Ovary (CHO) cells (Lee et al., 1976; Ellis et al., 1978b). A dominant lethal assay with rats was negative (Ellis et al., 1978b).

Trinitroglycerol was not carcinogenic in 2-year bioassays with dogs and mice; however, hepatocellular carcinoma was detected in male and female Charles River CD rats (Ellis et al., 1978a). Based on the rat hepatocellular carcinomas a potency factor of $1.66 \times 10^{-2} \text{ (mg/kg/day)}^{-1}$ was derived by the 100% model (USEPA, 1987a). Assuming daily water ingestion of 2 liters by 70 kg adults over a 70 year lifespan, one excess cancer per one million people (10^{-6}) could occur when the TNG concentration in the drinking water is 0.0021 mg/L (2.1 µg/L). One excess cancer per one-hundred-thousand (10^{-5}) or ten thousand people (10^{-4}) could occur at TNG concentrations of 0.021 mg/L (21 µg/L) and 0.21 mg/L (210 µg/L), respectively. By other cancer models, drinking water concentrations associated with an excess cancer risk of 10^{-6} are 2.0 µg/L, 12.0 µg/L, 0.4 µg/L, and 0.1 µg/L for the one-hit, probit, logit, and Weibull models, respectively (USEPA, 1987a). Trinitroglycerol does not have an EPA cancer classification.

Nitrocellulose

Nitrocellulose (NC), or cellulose trinitrate, consists of chains of glucose linked to form nitrate esters (Sullivan et al., 1978). It is a principle ingredient of propellants, smokeless powders, rocket fuel, mortar increments, and some explosives (Rosenblatt et al., 1973). Theoretically, a mixture is possible of

potential drinking water sources that receive wastewater discharges from NC production sources. However, human toxicity from water and any other exposure has not been reported.

Health advisory values are not established for NC because it was non-toxic at all doses studied and in all species (dogs, rats, mice) tested, and failed to be digested and absorbed in all species (USEPA, 1987b). Nitrocellulose was not toxic in mice and rats provided single acute doses up to 5,000 mg/kg (Lee et al., 1975). Similarly, it was not toxic in dogs, rats, and mice fed NC in proportions up to 10% of the diet for 13-weeks (Ellis et al., 1976). Some deaths occurred in the high-dose mice from blockage in the lower gastrointestinal tract in the regions where water is removed from the chyme. Deaths by the same mechanism occurred in control mice fed non-nitrated 10% cotton-linters in the diet. Dogs, rats, and mice fed NC in the diet at doses up to 3874, 1422, and 6056 mg/kg/day, respectively, for up to 24 months did not exhibit any treatment related toxicity (Ellis et al., 1980).

Nitrocellulose was not mutagenic in several strains of *S. typhimurium* with or without metabolic activation, and genotoxicity was not demonstrated in bone marrow cells, kidney cells, and lymphocytes from rats fed NC for 13-weeks or 2-years (Ellis et al., 1976). Treatment related carcinogenicity was not observed in dogs, rats, or mice fed NC in the diet for 12 or 24 months (Ellis et al., 1980). Nitrocellulose does not have an EPA cancer classification.

Hexahydro-1,3,5-trinitro-1,3,5-triazine

Hexahydro-1,3,5-trinitro-1,3,5-triazine is an explosive polynitramine that has been used as a high-impact explosive in military munitions and as a rat poison (ACGIH, 1986; Windholz, 1983). Commonly referred to as RDX (a British code name for Research Department Explosive or Royal Demolition Explosive), other synonyms include cyclonite, T₄, and cyclotrimethylenetrinitramine. Humans may be exposed to RDX occupationally by inhalation and dermal absorption when it is manufactured or incorporated into munitions at load, assembly, and pack (LAP) facilities (Kaplan et al., 1965; ACGIH, 1986). Potential environmental exposure could occur from drinking water sources contaminated by wastewater from RDX manufacturing and munitions LAP operations (Sullivan et al., 1979b). There are several reports of ingestion and inhalation exposures to RDX (Ketel and Hughs, 1972; Hollander and Colbach, 1969; Stone et al., 1969; Knepshild and Stone, 1972; Merrill, 1968; Woody et al., 1985, 1986). The later was by soldiers who burned composition C-4 (91% RDX) to heat food in the field. Effects from such exposures have been reported to include convulsions, unconsciousness, mental confusion, headache, fever, dizziness, nausea, vomiting, neuromuscular irritability, gastrointestinal symptoms, hematuria, and oliguria.



The one- and ten-day HAs for a child and the longer-term HA for a child have the same value, 0.1 mg/L (USEPA, 1988a). The longer-term HA for an adult is 0.4 mg/L and the lifetime HA is 0.002 mg/L. The one- and ten-day and the longer-term values are based upon neurological effects observed in cynomolgus monkeys that were fed RDX in their diets for 90 days (Martin and Hart, 1974). A NOAEL of 1 mg/kg/day and a LOAEL of 10 mg/kg/day for convulsions were determined. There were no studies considered appropriate for deriving one- and ten-day advisories; therefore, the longer-term advisory for a child was adopted as a conservative estimate for the shorter-term advisories. The lifetime HA was derived from effects in rats fed RDX in the diet for 24 months (Levine et al., 1983a). Suppurative inflammation of the prostate in male rats was the basis for a LOAEL of 1.5 mg/kg/day, and a NOAEL of 0.3 mg/kg/day. The lifetime advisory incorporates an additional uncertainty factor of 10 to account for RDX's possible carcinogenicity.

RDX was not mutagenic in several strains of *S. typhimurium* and in *S. cerevisiae* with and without metabolic activation (Cholakis et al., 1980; Whong et al., 1980; Simmon et al., 1977). It was negative also in a dominant lethal assay with F344 rats and an unscheduled DNA (UDS) assay with human diploid fibroblasts with and without metabolic activation (Cholakis et al., 1980; Dilley et al., 1978).

RDX was not carcinogenic when fed to Sprague-Dawley and F344 rats in the diet for 2 years (Levine et al., 1983; Hart, 1977). Lish et al. (1984), however, did find that female B6C3F₁ mice developed hepatocellular carcinomas and adenomas when fed RDX. The female mouse data was used to calculate a potency factor of 1.1×10^{-1} (mg/kg/day)⁻¹ by the LMS model (USEPA, 1988a). Assuming daily water ingestion of 2 liters by 70 kg adults over a 70 year lifespan, one excess cancer per one million people (10^{-6}) could occur when the RDX concentrations in the drinking water is 0.0003 mg/L (0.3 µg/L). One excess cancer per one-hundred-thousand (10^{-5}) or ten-thousand people (10^{-4}) could occur at RDX concentrations of 0.003 mg/L (3.0 µg/L) and 0.03 mg/L (30.0 µg/L), respectively. By other cancer models, drinking water concentrations associated with an excess cancer risk of 10^{-6} are 0.3 µg/L for the one-hit model and less than 0.002 µg/L for the other models (one-hit, multihit, probit, logit, and Weibull) (USEPA, 1988a). RDX is classified as an EPA Group C (possible human carcinogen) contaminant.

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine is an explosive polynitramine that has been used to implode fissionable material in nuclear devices to achieve critical mass, and as a component in plastic-bonded explosives, solid-fuel rocket propellants and in military munitions (Sullivan et al.,

Wright, Kitchens et al., 1979). Commonly referred to as HMX (for High Melting explosive), other synonyms include cyclotetramethylenetetranitramine, Octogen, and RRL. Humans may be exposed to HMX occupationally by inhalation and dermal absorption when it is manufactured or incorporated into munitions at manufacturing, assembly, and pack (LAP) facilities. Potential environmental exposure could occur from drinking water sources contaminated by wastewater from HMX manufacturing and munitions LAP operations (Sullivan et al., 1979b). The only health effects reported in humans is skin irritation in volunteers exposed to solid HMX in a patch test (Rych et al., 1984).

The one- and ten-day HAs for a child and the longer-term HA for a child are the same value, 5 mg/L (USEPA, 1988b). The longer-term HA for an adult is 20 mg/L and the lifetime HA is 0.4 mg/L. All of the advisory values are based upon a rat (F344 strain) 90-day feeding study by Everett et al. (1985). The NOAEL was 50 mg/kg/day and the LOAEL was 115 mg/kg/day for liver lesions, characterized by enlarged centrilobular cells with pale nuclei, in male rats. There were no studies considered appropriate for deriving one- and ten-day advisories; therefore, the longer-term advisory for a child was adopted as a conservative estimate for the shorter-term advisories.

Genotoxicity studies are limited to mutagenicity assays with several strains of *S. typhimurium* and to a mitotic gene conversion assay with *S. cerevisiae* (Johnson et al., 1977; Stilwell et al., 1977; Whong et al., 1980). HMX was negative in all of the studies, but the results were considered inconclusive because of the low concentrations that were assayed or the lack of data reported (USEPA, 1988b).

There were no carcinogenicity studies found in the literature; therefore, HMX is classified as an EPA Group D (not classifiable as to human carcinogenicity) contaminant.

2.1.2. 2,4,6-Trinitrotoluene

2,4,6-Trinitrotoluene (TNT), also known as alpha-trinitrotoluol and alpha-trinitrotoluenes, had wide application in shells, bombs, grenades, demolition explosives, and propellant compositions (Castorina, 1980; Department of the Army, 1967). Deaths and toxicity in humans has been primarily by dermal and inhalation occupational exposure. There are a variety of health effects associated with TNT exposure, but toxic hepatitis (jaundice) and aplastic anemia are the principle causes of death (Zakhari and Villaume, 1978). Other TNT effects include respiratory and skin irritation, gastrointestinal disorders, cataract formation, menstrual disorders, neurological disorders, nephrotoxicity, and hematological effects.

The one- and ten-day HAs for a child and the longer-term HA for a child

and adult have the same value, 0.02 mg/L (USEPA, 1989c). The lifetime HA is 0.002 mg/L. All of the advisory values are derived from a study where dogs were fed TNT in the diet for 26 weeks (Levine et al., 1983b). The LOAEL for the study is 0.5 mg/kg/day for the occurrence of hepatocytomeglia. There were no studies considered appropriate for deriving one- and ten-day advisories; therefore, the longer-term advisory for a child was adopted as a conservative estimate for the shorter-term advisories. The lifetime advisory incorporates an additional uncertainty factor of 2 to account for TNT's possible carcinogenicity.

Trinitrotoluene was found to be mutagenic in several strains of *S. typhimurium* with and without metabolic activation (Ellis et al., 1978; Dilley et al., 1978b). It was negative in all mammalian genotoxicity assays which included an *in vivo* assay of bone marrow cell from treated rats, an *in vitro* Unscheduled DNA synthesis (UDS) assay with human diploid fibroblasts, a mouse bone marrow micronucleus assay, and an *in vivo/in vitro* UDS assay with rat hepatocytes (Dilley et al., 1978; Ashby et al., 1985).

Two year bioassays for carcinogenicity were conducted with Fischer 344 rats and hybrid B6C3F₁ mice (Furedi et al., 1984a-f). Female rats were positive for urinary bladder papillomas. There were no statistically significant treatment related cancers in male rats or in male and female mice. The female rat data was used to calculate a potency factor of 3×10^{-2} (mg/kg/day)⁻¹ by the LMS model (USEPA, 1989c). Assuming daily water ingestion of 2 liters by 70 kg adults over a 70 year lifespan, one excess cancer per one million people (10^{-6}) could occur when the TNT concentrations in the drinking water is 0.001 mg/L (1 µg/L). One excess cancer per one-hundred-thousand (10^{-5}) or ten-thousand people (10^{-4}) could occur at TNT concentrations of 0.01 mg/L (10 µg/L) and 0.1 mg/L (100 µg/L), respectively. By other cancer models, drinking water concentrations associated with an excess cancer risk of 10^{-6} are 0.7 µg/L, 20 µg/L, 700 µg/L, 20 µg/L, and 10 µg/L for the one-hit, multihit, probit, logit, and Weibull models, respectively (USEPA, 1989c). Trinitrotoluene is classified as an EPA Group C (possible human carcinogen) contaminant.

Diisopropyl Methylphosphonate

Diisopropyl methylphosphonate (DIMP) is produced during the manufacture of the nerve gas isopropyl methylphosphonofluoridate (GB or Sarin) (Rosenblatt et al., 1975). It is a production by-product and is not a metabolite or degradation product. Potential human exposure to DIMP is thought to be limited to contaminated groundwater in the area of Rocky Mountain Arsenal, Colorado. Skin irritation is the only effect from DIMP exposure to humans that has been reported (Thoburn and Gunter, 1981). However, those who developed rashes also were exposed simultaneously to a variety of other organic substances.



The one- and ten-day HAs for a child and the longer-term HA for a child have the same value, 8 mg/L (USEPA, 1989d). The longer-term HA for an adult is 30mg/L and the lifetime HA is 0.6 mg/L. The advisory values are derived from a study where dogs were fed DIMP in the diet for 90 days (Hart, 1980). There were no DIMP related effects in the animals fed the chemical up to doses of 75 mg/kg/day, the highest dose tested. Similarly, there were no treatment related effects in rats, mice, and mink fed DIMP in the diet (Hart, 1976; Hart, 1980; Aulerich et al., 1979; Biskup et al., 1978; Hardisty, 1976). The 75 mg/kg/day NOAEL from the dog study was selected as a conservative NOAEL for calculating HA values. There was no LOAEL because DIMP mediated effects were not observed in any of the species tested. There were no studies considered appropriate for deriving one- and ten-day advisories; therefore, the longer-term advisory for a child was adopted as a conservative estimate for the shorter-term advisories.

Diisopropyl methylphosphonate was negative in microbial genotoxicity studies with several strains of *S. typhimurium* and a strain of *S. cerevisiae* with and without metabolic activation (Hart, 1980). Additional genotoxicity studies have been completed since the DIMP HA was published. These include the following assays: *Salmonella*/Ames test, sister chromatid exchange in Chinese Hamster Ovary cells, chromosome aberration in Chinese Hamster Ovary cells, DNA damage testing in Chinese Hamster Ovary cells, mouse lymphoma mutagenesis, bone marrow micronucleus in rats and mice, and *in vivo* testing in rats and mice ((Tice, 1990a, 1990b, 1991a-g). Chromosomal aberrations were observed in Chinese Hamster cells with and without metabolic activation. The other tests were negative.

There were no carcinogenicity studies found in the literature; therefore, DIMP is classified as an EPA Group D (not classifiable as to human carcinogenicity) contaminant.

Nitroguanidine

Nitroguanidine is a nitramino compound that is presently used in triple-base propellant mixtures to produce flashless, less erosive formulations (Kenyon, 1982; Encyclopedia of Explosive and Related Items, 1974). Synonyms include alpha-nitroguanidine, beta-nitroguanidine, NG, NGu, and picrite. The abbreviation NQ is sometimes used in lieu of NG to prevent confusion with the explosive nitroglycerol. Humans may be exposed to NQ occupationally when it is manufactured or incorporated into munitions at load, assembly, and pack (LAP) facilities. Potential environmental exposure could occur from drinking water sources contaminated by wastewater from NQ manufacturing and munitions LAP operations (Kaplan et al., 1982). No studies on the health effects of NQ in humans have been reported.



The one- and ten-day HAs for a child and the longer-term HA for a child have the same value, 11 mg/L (USEPA, 1990a). The longer-term HA for an adult is 37mg/L and the lifetime HA is 0.74 mg/L. The one- and ten-day values are based upon increased water consumption, decreased electrolytes, and decreased heart weights in Sprague-Dawley rats that were fed NQ in their diets for 14 days (Morgan et al., 1988a). The NOAEL in the 14-day study is 316 mg/kg/day and the LOAEL is 1000 mg/kg/day. There were no studies considered appropriate for deriving a one-day advisory; therefore, the ten-day advisory for a child was adopted as a conservative estimate for the shorter-term advisory. The longer-term and lifetime advisories were derived from effects in Sprague-Dawley rats fed NQ in the diet for 90 days (Morgan et al., 1988b). Decreased body weight and increased brain-to-body weight ratios in female rats, and increased water consumption in male and female rats were the basis for a LOAEL of 1000 mg/kg/day and a NOAEL of 316 mg/kg/day. All of the advisory values incorporated an additional factor of 3 to account for uncertainty introduced by equivocal evidence of developmental toxicity in rabbits (Coppes et al., 1988).

There was no evidence of NQ genotoxicity in microbial assay systems with *S. typhimurium*, *S. cerevisiae* and *Escherichia coli* with and without metabolic activation (Ishidate and Odashima, 1977; Kaplan, 1982; Sebastian and Korte, 1988; McGregor et al., 1980; Kenyon, 1982; Brusick and Matheson, 1978). Nitroguanidine was not mutagenic in assays with mouse lymphoma cells and Chinese Hamster Ovary cells with and without metabolic activation (Harbell and Korte, 1987; Harbell et al., 1988). There was no mutagenic potential demonstrated in a sexed-linked recessive lethal mutation assay with *Drosophila melanogaster* (Gupta et al., 1988). Brusick and Matheson (1978) did not demonstrate a clastogenic response in dominant lethal assays with mice and rats; however, Ishidate and Odashima (1977) reported that NQ was a clastogen for Chinese Hamster fibroblast (lung) cells. The conclusions of the later study may be compromised by deficiencies in methodology (USEPA, 1990a).

There were no carcinogenicity studies found in the literature; therefore, NQ is classified as an EPA Group D (not classifiable as to human carcinogenicity) contaminant.

White Phosphorus

White phosphorus (WP), also known as elemental phosphorus and yellow phosphorus, has been used as a military screening smoke and in incendiary devices. Because of its extreme toxicity, WP is no longer used in matches, fireworks, and as a rodenticide; however, there is continued use in analytical chemistry, manufacture of phosphorus compounds, and in the semiconductor and electroluminescent industries (Brown et al., 1981; Hawley, 1981). Humans can be exposed occupationally, which was more prevalent in the early 1900's when WP was used in the match and fireworks industry, and from the environment from waste effluent from manufacture and production (Ward, 1926;

Hughes et al., 1962; Sullivan et al., 1979c). Symptoms of acute WP poisoning include gastrointestinal pain, nausea, vomiting, shock, luminescent vomitus and feces (described as the "smoking stool syndrome"), hepatotoxicity, nephrotoxicity, neurotoxicity, and changes in the hematopoietic system (Rubitsky and Myerson, 1949; Simon and Pickering, 1976). Progressive necrotic bone degeneration is a major effect from WP exposure reported, in the earlier literature, to occur primarily in the facial bones (thus the name "phossy jaw") (Hughes et al., 1962; Ward, 1926).

Only a lifetime health advisory value of 0.0001 mg/kg/day is recommended for WP (USEPA, 1990b). A minimum lethal dose of 1 mg/kg has been reported, and death has occurred following the ingestion of as little as 8 mg (0.1 mg/kg for a 70 kg adult) and at 3 mg (0.3 mg/kg for a 10 kg child) (Brewer, 1958; Heiman, 1946). Due to its extreme toxicity following oral ingestion and the lack of additional data, one- and ten-day and longer-term advisories are not recommended. The lifetime advisory is based on the occurrence of mortality during parturition in female Sprague-Dawley rats administered WP in corn oil by gavage. The NOAEL for the study is 0.015 mg/kg/day and the LOAEL is 0.075 mg/kg/day.

There were no carcinogenicity studies found in the literature; therefore, WP is classified as an EPA Group D (not classifiable as to human carcinogenicity) contaminant.

1,3-Dinitrobenzene

1,3-Dinitrobenzene (DNB) is a by-product in the manufacture of trinitrotoluene, is an intermediate in the production of phenylenediamine (a dye intermediate), is used in organic synthesis, and as a camphor substitute in celluloid production (USEPA, 1985). Synonyms include *m*-dinitrobenzene, *m*-DNB, and 1,3-DNB. Sources of human exposure are occupational and environmental (USEPA, 1985; Okubo and Shigeta, 1982; Ishihara, 1976). Environmental sources occur from production and manufacture wastewater effluents. Effects reported to occur in humans include cyanosis, methemoglobinemia, anemia, palpitations, dizziness, fatigue, and hemolytic jaundice (Gleason et al., 1986; Okubo and Shigeta, 1982; Ishihara, 1976).

The one- and ten-day HAs for a child and the longer-term HA for a child have the same value, 0.04 mg/L (USEPA, 1991a). The longer-term HA for an adult is 0.14 mg/L and the lifetime HA is 0.001 mg/L. The advisory values are derived from a study where Carsworth Farm rats were administered DNB in drinking water for 16 weeks (Cody et al., 1981). The NOAEL is 0.4 mg/kg/day and the LOAEL is 1.14 mg/kg/day for effects on the spleen (hemosiderin deposition) and testes (reduced weight and spermatogenesis). There were no studies considered appropriate for deriving one- and ten-day advisories;



therefore, the longer-term advisory for a child was adopted as a conservative estimate for the shorter-term advisories.

There are mixed results for mutagenicity in assays with *S. typhimurium*; however, the majority of the assays show DNB to be mutagenic with and without metabolic activation (Spanggord et al., 1982; McGregor et al., 1980; Kawai et al., 1987; Chiu et al., 1978; Garner et al., 1977; Probst et al., 1981). In the presence or absence of metabolic activation, there was no DNB induced mitotic gene conversion in *S. cerevisiae* and no effect to DNA repair in *E. coli* (McGregor et al., 1980). Unscheduled DNA synthesis (UDS) was not increased in cultivated hepatocytes by DNB (Probst et al., 1981).

There were no carcinogenicity studies found in the literature; therefore, DNB is classified as an EPA Group D (not classifiable as to human carcinogenicity) contaminant.

Hexachloroethane

Hexachloroethane (HCE) is a chlorinated alkane that has been used by the military, in combination with zinc oxide and aluminum, in pyrotechnic devices and as a screening smoke. It has several nonmilitary uses such as in the production of fluorocarbon, and in formulations of lubricants, pesticides, fire extinguishing fluids, paper, wood, and paints (Sax, 1986; Kitchens et al., 1978). Synonyms include carbon hexachloride, pentachloroethane, hexachlorethylene, diskotal, falkitol, and phenohep. Sources of human exposure are occupational and environmental from military and industrial uses and during its manufacture (Kitchens et al., 1978). Health effects in humans exposed to heated HCE include neurotoxicity, photophobia, and eye irritation, tearing, and inflammation (Grant, 1986).

The one- and ten-day HAs for a child have the same value, 5 mg/L (USEPA, 1991b). The longer-term HA for a child is 0.1 mg/L and the longer-term HA for an adult is 0.5 mg/L. The lifetime HA is 0.001 mg/L. The one- and ten-day advisory values are derived from a study with CDF F344 rats that were fed HCE in the diet for 16 days (Gorzinski et al., 1980a). The NOAEL for the 16-day study is 50 mg/kg/day and the LOAEL is 200 mg/kg/day for hepatic necrosis and decreases in body weight gain. There were no studies considered appropriate for deriving a one-day advisory; therefore, the ten-day advisory for a child was adopted as a conservative estimate for the one-day advisory. The longer-term and lifetime advisories are based upon a study with CDF F344 rats that were fed HCE in the diet for 16 weeks (Gorzinski et al., 1980b). The NOAEL for the 16-week study is 1.3 mg/kg/day and the LOAEL is 20 mg/kg/day for liver (hepatocytomeglia) and kidney (renal tubular atrophy and degeneration) lesions. The lifetime advisory incorporates an additional uncertainty factor of 10 to account for HCE's possible carcinogenicity.

Genotoxicity studies for HCE are limited to assays in microbial systems. Mutagenicity was not demonstrated, with and without metabolic activation, in all strains of *S. typhimurium* tested and an assay with *S. cerevisiae* was negative (Simmon and Kauhanen, 1978; Weeks et al., 1979; Nakamura et al., 1987).

Two-year cancer bioassays were conducted with Osborne-Mendel rats and B6C3F₁ mice that were administered HCE in corn oil by gavage (NCI, 1978). Male and female mice were positive for hepatocellular carcinoma. There were no statistically significant treatment related cancers in the rats. Renal carcinomas and adenomas were observed in male F344 rats administered HCE in corn oil by gavage in a lifetime study (NTP, 1989). The mouse data from the NCI (1978) study was used to calculate a potency factor of 1.4×10^{-2} (mg/kg/day)⁻¹ by the LMS model (USEPA, 1991b). Assuming daily water ingestion of 2 liters by 70 kg adults over a 70 year lifespan, one excess cancer per one million people (10^{-6}) could occur when the HCE concentration in the drinking water is 0.003 mg/L (3 µg/L). One excess cancer per one-hundred-thousand (10^{-5}) or ten-thousand people (10^{-4}) could occur at HCE concentrations of 0.03 mg/L (30 µg/L) and 0.3 mg/L (300 µg/L), respectively. By other cancer models, drinking water concentrations associated with an excess cancer risk of 10^{-6} are 1 µg/L, 200 µg/L, 5000 µg/L, 50 µg/L, and 2 µg/L for the one-hit, multihit, probit, logit, and Weibull models, respectively (USEPA, 1991b). Hexachloroethane is classified as an EPA Group C (possible human carcinogen) contaminant.

Summary

Since the initiation of the cooperative program between the Army and the EPA, ten munitions drinking water HAs have been published. They include advisories for trinitroglycerol; nitrocellulose; hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX); octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX); 2,4,6-trinitrotoluene (TNT); diisopropyl methylphosphonic acid (DIMP); nitroguanidine; white phosphorus; 1,3-dinitrobenzene; and hexachloroethane (see Table 2). The effects for the individual chemicals, as reflected by the advisory values, range from being completely nontoxic when ingested in drinking water (e.g., nitrocellulose) to being extremely toxic at very low concentrations (e.g., white phosphorus).

Most of the advisory values are based on effects observed in animal studies, but considered relevant to humans. The one exception is trinitroglycerol which is based on a pharmacological effect in humans. All of the advisory values are calculated from a NOAEL or a LOAEL for systemic effects which include body and organ weight changes and/or organ histopathology. Cancer studies have been reported for only four of the munitions: TNT, RDX, hexachloroethane, and trinitroglycerol.



TABLE 3. NTIS^a Accession Numbers for Munitions Drinking Water Health Advisories

Chemical	NTIS Accession Number
o Trinitroglycerol	PB90-273558-AO5/AO1 ^b
o Nitrocellulose	PB90-273541-AO3/AO1
o Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	PB90-273553-AO5/AO1
o Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	PB90-273525-AO5/AO1
o 2,4,6-Trinitrotoluene (TNT)	PB90-273566-AO6/AO1
o Diisopropyl Methylphosphonic Acid (DIMP)	PB90-273517-AO4/AO1
o Nitroguanidine	PB90-273509-AO5/AO1
o White Phosphorus	PB91-161026/AS-AO5/AO1
o 1,3-Dinitrobenzene	PB91-159640-AO5/AO1
o Hexachloroethane	PB91-159657-AO4/AO1

^a/ National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

^b/ - AO"X"/AO"X" are suffixes for Paper copy/Microfiche copy

All of the munitions health advisories are available to the public and may be obtained from the National Technical Information Service (NTIS), Alexandria, VA (accession numbers are listed in Table 3). Health advisories for other Army environmental contaminants are in various stages of preparation and will be published in the future. These include: zinc chloride; dimethyl methylphosphonate; 2,4-/2,6-dinitrotoluene; isopropyl methyl phosphonic acid; 1,4-dithiane; and *p*-chlorophenylmethyl sulfide/sulfone/ sulfoxide.

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Application of the Powdered Activated Carbon/Activated Sludge
(PACT) and Wet Air Oxidation Processes to the Treatment of Explosives
Contaminated Wastewaters

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INTRODUCTION

Army ammunition plant (AAP) waste waters contain low levels of explosives and explosives components such as TNT, DNT, RDX, HMX, NG, NC and related by-products and intermediates. These are either biodegraded with difficulty, biotransformed into more toxic materials, or remain unaffected when subjected to conventional biological treatment. Due to the toxicity of these substances and the biotransformation products, effluent guidelines have been recommended, as indicated in Table 1. It is pointed out that DNT is both a known carcinogen and an EPA priority toxic pollutant. These numbers are advisory only and are not yet legally enforceable Federal Standards, but do indicate a growing concern about their discharge into receiving waters.

TABLE 1
***Effluent Guidelines For Explosives
Components In Receiving Water***

	Solubility mg/L	Concentration	
		mg/L ^b	mg/L ^c
2,4,6 - TRINITROTOLUENE (TNT)	120	0.135	0.002
CYCLONITE (RDX)	25	0.105	0.002
HMX	5	1.7	0.400
2,4 - 2,6 - DINITROTOLUENE (DNT) ^a	300	0.0007	
NITROGLYCERIN (NG)	1,800		0.005
NITROCELLULOSE (NC)	1	-	

a - KNOWN CARCINOGEN, ON EPA's PRIORITY TOXIC POLLUTANT LIST

b - (OR PPM), RECOMMENDED BY THE SURGEON GENERAL IN EARLY 80's

c - HEALTH ADVISORY LIMITS ESTABLISHED BY EPA FOR DRINKING WATER
IN NOVEMBER 1988 AND JANUARY 1989

- NO KNOWN TOXICITY



The only known means of removing these substances (except NC) from wastewater is via granular activated carbon (GAC) adsorption. However, attainment of the desired removal will be very expensive and there will be a need to dispose of large quantities of hazardous waste (spent GAC).

The Army currently has two major propellant and explosive (P&E) manufacturing plants in operation, Holston AAP (HSAAP) and Radford AAP (RAAP).

HSAAP is the only DOD plant manufacturing RDX, HMX and related explosives. As a result of its manufacturing operations, TNT, RDX, HMX, SEX and TAX are discharged from HSAAP's wastewater treatment plant. However, the state of Tennessee has not yet placed limits on these substances, as they are discharged into the fast-flowing Holston River. A second RDX plant was planned for construction at Louisiana AAP. The effluent here would have been discharged to a sensitive recreational lake and was definitely a target for abatement, but construction of this facility was cancelled in 1990.

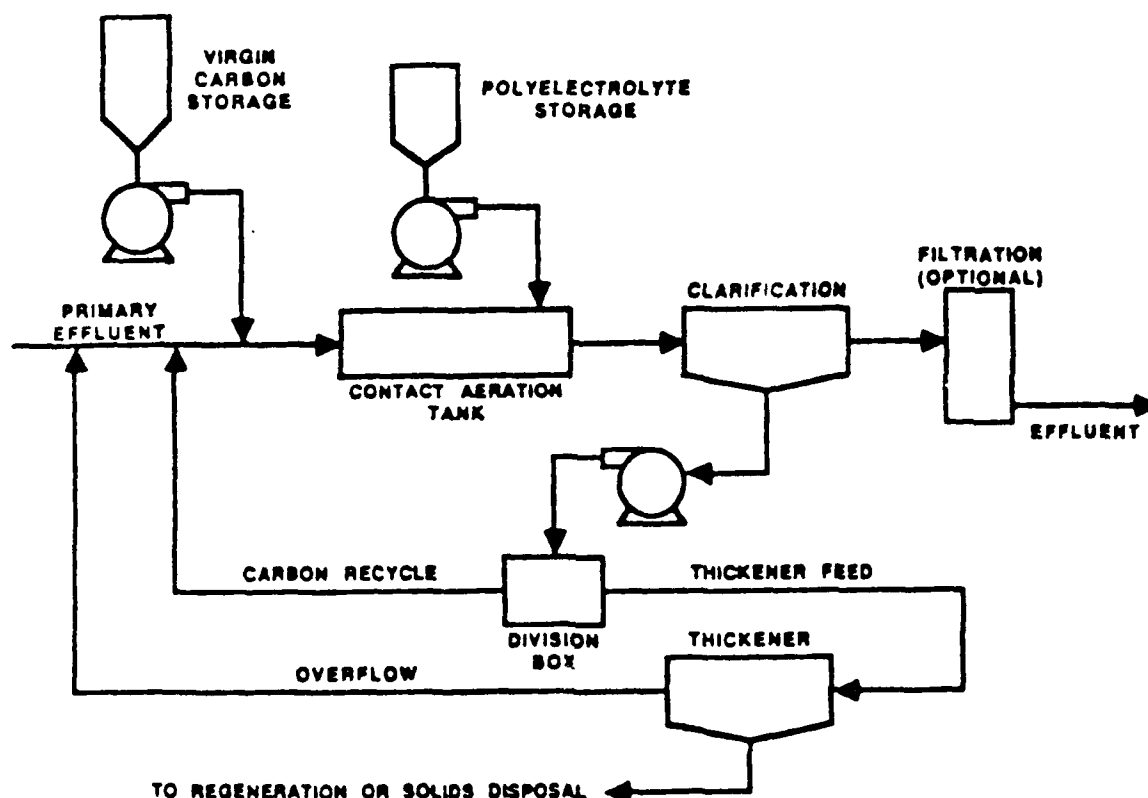
RAAP is a diversified P&E manufacturer, including NC and NC-based propellants. These ventures have resulted in the manifestation of serious problems with the discharge of NC, NG and DNT. In addition, consideration is currently being given to re-instituting TNT manufacture; last produced in 1985. This is complicated by the lack of a satisfactory on-site method of treating red water, a hazardous waste by-product of TNT purification, to comply with increasingly stringent environmental regulations, as well as problems with adequate removal of DNT and TNT from the manufacturing wastewaters.

DESCRIPTION OF THE PACT AND WAO PROCESSES

The powdered activated carbon (PAC)-activated sludge (PACT) and wet air oxidation (WAO) processes are potentially attractive alternatives for the treatment of P&E manufacture wastewaters and red water generated during the manufacture of TNT. The PACT process is widely used in the United States and other countries, with or without WAO, and numerous installations are operational in the United States for the treatment of municipal and highly toxic organic industrial wastes. In addition, these processes are widely used for the treatment and removal of toxics and priority pollutants from contaminated groundwaters at Superfund sites. However, the PACT and WAO processes have not yet been applied to the treatment of wastewaters common to AAP's engaged in the manufacture or load and pack (LAP) of P&E.

The PACT wastewater treatment system incorporates the addition of PAC to the aeration basin of a biological activated sludge system. A schematic of the PACT process is shown in Figure 1. This combination of physical adsorption with biological oxidation and assimilation has been proven to be particularly effective in treating wastewaters which are variable in concentration and composition, highly colored, or contain materials which are nonbiodegradable or potentially toxic to biological growth. Characteristic

FIGURE 1 - PACT WASTEWATER TREATMENT PROCESS
GENERAL PROCESS DIAGRAM



advantages of the PACT wastewater treatment system, compared to conventional activated sludge treatment include:

1. Improved BOD and COD removals
2. Stable operation with variable influent concentrations and flow rates
3. Enhanced removal of toxic substances and priority pollutants
4. Effective color removal
5. Improved sludge settleability and dewaterability
6. Suppressed stripping of volatile compounds, including odor control

The PACT adsorption and activated sludge processes appear to have a synergistic effect on each other, with enhanced physical adsorption and biological assimilation, resulting in extremely high (99+%) removals on concentrated, difficult-to-biodegrade waste streams. This synergism is explained by microscopic observations made at the University of Wisconsin. (Ref. 1) In these studies it was observed that bacteria of the ubiquitous

species *pseudomonas aeruginosa* and *P. cepacia*, which are nutritionally versatile organisms capable of oxidizing about any type of ring compound, were associated with or attached to the carbon particles in PACT systems. The PAC also absorbs oxygen and difficult-to-biodegrade organics that are held in place in intimate contact with the bacteria for ultimate biodegradation and oxidation. Since the bacteria are attached to the carbon particles, the conserved motive energy is directed toward assimilation of organics. These interactions allow difficult-to-biodegrade organics to remain within the active biosystem for a time period closer to the solids residence time than the hydraulic detention time.

PAC, because of its greater specific surface area than GAC, will absorb a greater amount of organics than GAC. PAC is also only about 1/2 the cost of GAC and incorporation into the activated sludge process eliminates the need for expensive carbon columns. In addition PAC is more amenable to regeneration by WAO than GAC is by state-of-the-art GAC regeneration processes. The major problem with GAC regeneration is attrition of a considerable fraction of the GAC to unusable fines; that problem does not exist with WAO regeneration of PAC.

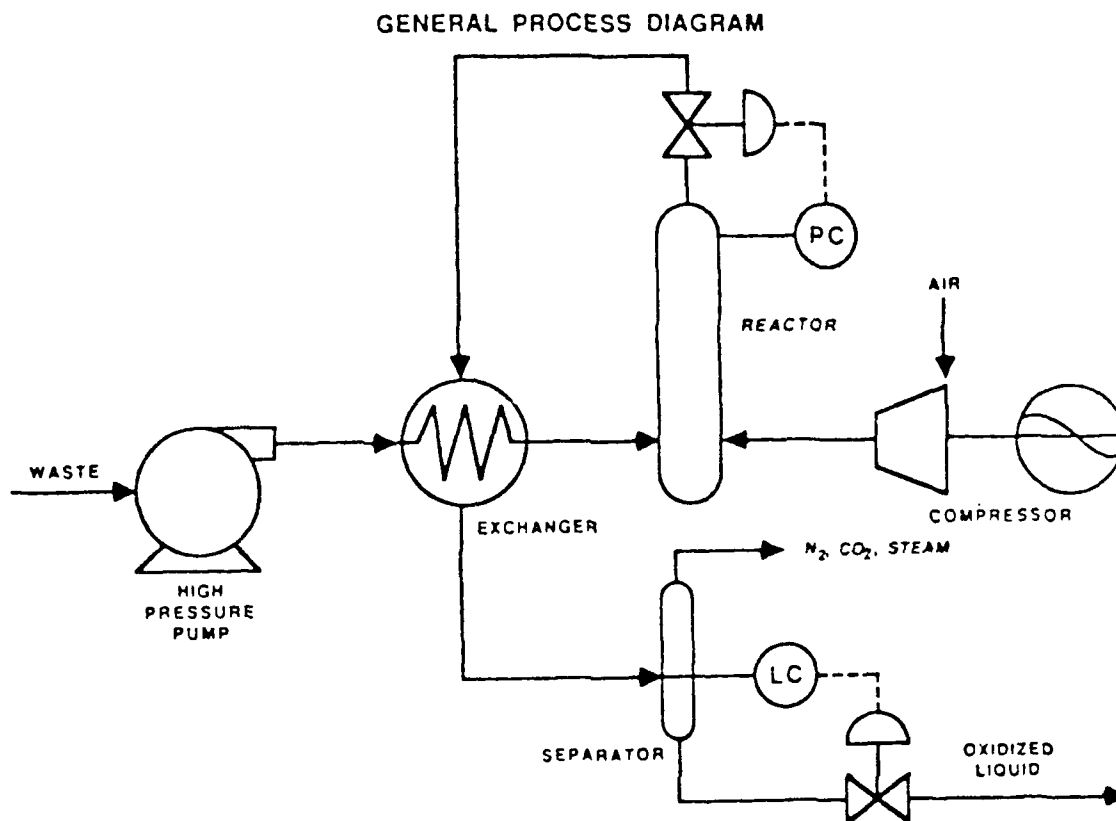
The high solids content of the activated sludge liquor with PAC allows long sludge retention time with decreased hydraulic detention time, both conditions being advantageous to decreasing the size of the activated sludge tanks. The addition of the solids also aids in improving settling characteristics of sludge, especially difficult-to-settle sludges, such as gelatinous or filamentous masses.

The WAO process complements the PACT process by oxidizing the sludge, destroying the absorbed organics, regenerating the carbon, and returning the regenerated carbon to the PACT unit. WAO is the aqueous phase oxidation at elevated pressures and temperatures of organic and inorganic materials, and is illustrated by Figure 2. Operating conditions for the hydrolysis and oxidation reactions that take place are pressures of 300 to 3000 psig and temperatures of 175 to 320°C (347 to 608°F). At these conditions the high solubility of oxygen provides a positive driving force for complete oxidation. Also, water is in the liquid state, which catalyzes the reactions so that they proceed at much lower temperatures than open flame oxidation, while providing a medium for heat transfer and heat removal by evaporation.

WAO is an ideal process for the treatment of wastes whose solids content (dissolved plus suspended) is too low for conventional incineration. Except for the initial process start-up when external heat must be supplied to bring the reactor contents to reaction temperature, the WAO reaction is autogenous as long as feed COD concentrations exceed approximately 15,000 mg/L. After start-up, heat generated by the oxidation reactions is used to raise the temperature of the feed stream to the reaction temperature. The products of the oxidations are carbon dioxide, water and nitrogen, or ammonia, (no SO_x and NO_x), with solids (dissolved or suspended) being converted to their highest oxidative state.



FIGURE 2 - WET AIR OXIDATION PROCESS

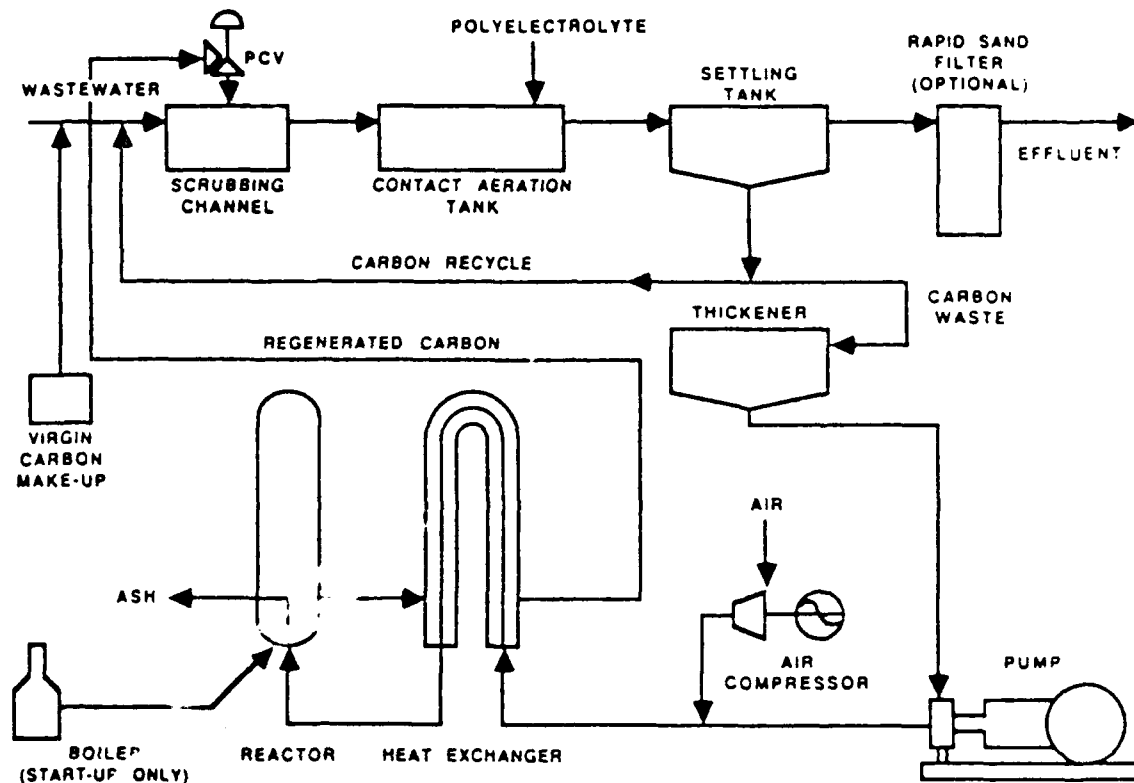


When WAO is used in conjunction with PACT to treat the wasted PACT sludge, regenerated carbon is recycled back to the PACT unit from the WAO unit as shown in Figure 3. As a result, the only process influents are the wastewater feed and virgin PAC make-up (about 5-10%) and the only effluents are the treated wastewater, a very small amount of inorganic ash and largely innocuous gases.



FIGURE 3 - ZIMPRO PACT/WAO PROCESS

GENERAL PROCESS DIAGRAM



EVALUATION OF PACT AND WAO PROCESSES FOR THE TREATMENT OF P&E MANUFACTURE WASTEWATERS

Prior to the cancellation of the RDX Expansion Plant project, PACT/WAO was one of the wastewater treatment options being considered for this facility. In support of this project a feasibility study to determine the efficacy of treating RDX manufacture wastewater with the PACT and WAO processes was successfully completed by Zimpro Passavant Inc. (ZPI). (Ref. 2) Two bench-scale PACT pilot units were operated for 54 days using actual HSAAP wastewater at a feed flow rate of 5 liters/day. The units simulated the HSAAP ILWTF treatment scheme of denitrification, followed by aerobic treatment, with one unit utilizing anoxic denitrification as at HSAAP, and the other unit utilizing anaerobic denitrification. The sludge was subjected to oxidation in a titanium autoclave at 250°C for one hour to simulate WAO. Tables 2, 4 and 5 show the results of these tests.

The results of the PACT tests (Table 2), indicated better COD removal from the HSAAP wastewater than from HSAAP's ILWTF (Table 3), as well as very high total N removal, with both anoxic and anaerobic denitrification providing equivalent overall treatment. However, anaerobic treatment has

TABLE 2
Holston Army Ammunition Plant
PACT Study Summary of Analysis

ANALYSIS (a)	WASTE A	WASTE B	WASTE MIX (b)	SYSTEM I			SYSTEM II		
				ANAEROBIC EFFLUENT	CLARIFIER EFFLUENT	% REMOVAL	ANOXIC EFFLUENT	CLARIFIER EFFLUENT	% REMOVAL
COD	680.0	125.0	218.0	48.6	11.7	94.6	18.6	14.5	93.3
BOD	566.0	74.0	156.0	—	<6.0	>96.2	—	<6.0	>96.2
TKN	46.5	84.4	78.1	10.0	2.7	96.5	2.4	1.9	97.6
NH ₃	4.8	<1.0	<1.6	5.5	1.8	(c)	<1.0	1.0	(c)
NO ₃	0.9	2.3	2.1	1.8	7.1	(c)	2.1	2.6	(c)
TOTAL N	47.4	86.7	80.2	11.6	9.8	87.8	4.5	4.5	94.4

(a) ALL ANALYSES IN MG/L

(b) BASED ON 16.7 VOLUME % WASTE A AND 83.3 VOLUME % WASTE B

(c) DISREGARD DUE TO UNNECESSARY ADDITION OF NH₃ AS NUTRIENT

TABLE 3
RDX Manufacture Wastewater Characteristics
HOLSTON ARMY AMMUNITION PLANT

	ILWTF INFLUENT (mg/L)	ILWTF EFFLUENT (mg/L)	% REMOVAL	CURRENT NPDES RQMTS (mg/L)*	
				MONTHLY AVG	DAILY MAX
BOD	210.0	<4.0	>98.0	4.0	11.0
COD	250.0	<50.0	>75.0	45.0	122.0
TSS	<20.0	<12.0	~40.0	5.0	17.0
NH ₃ (as N)	5.0-10.0	0.01	99:9	2.7 (S)** 5.3 (W)**	5.3(S) 8.0(W)
TOTAL N (as N)	-	7.1		11.0(S) 18.0(W)	42.0(S) 42.0(W)
NO ₃ - NO ₂ (as N)	10.0-20.0	5.0-10.0	50.0	-	-
TOTAL PHOS (as P)	-	1.3	-	6.0	-
TNT	-	<0.05	-	(a)	-
RDX	4.7	2.6	44.7	(a)	-
TAX	2.5	0.07	97.2	(a)	-
SEX	1.4	1.3	7.1	(a)	-
HMX	1.8	1.8	11.1	(a)	-

* BASED ON FLOW RATE OF 4.5 MGD

** (S) 1 MAY - 31 OCT: (W) 1 NOV - 30 APR

(a) A BIOASSAY TEST SPECIFYING A 48 HOUR STATIC TOXICITY
USING DAPHNIA AND FAT HEAD MINNOWS IS REQUIRED

the disadvantages of not providing for solids washing and removal, expensive to operate, thus consideration of this mode of operation will be dropped in favor of the anoxic mode. Unfortunately, analyses for analysis of RDX, HMX, SEX and TAD were apparently mislabeled and valid test results were obtained. The probable removal was not confirmed in further tests. The analyses for RDX, HMX, SEX and TAD in WAO effluent were performed independently and showed that these materials were all below the detection level. However, due to the uncertainty of how much was present initially it could not be said that explosives absorbed on the PAC would be destroyed in the WAO. This would have to be evaluated further.

In the WAO test the biomass has been destroyed and 81 percent PAC has been regenerated, as indicated in Table 4. It is anticipated this figure could be increased to between 90 to 95 percent. The difference is attributable to experimental error due to the low flow rate and sample size.

Table 4 Sludge composition before and after wet air oxidation

	Before WAO	After WAO
Suspended solids, g/L	40.7	26.7
Suspended ash, g/L	10.3	8.6
Biomass, g/L	8.0	0.0
Carbon, g/L	22.4	18.1

Theoretically, the off-gas should contain only CO_2 , H_2O , and N_2 (condensable). Table 5 verifies this, with CO_2 and N_2 comprising 97.06% of the off-gas, or 97.06% after correcting for the excess O_2 present. The only remaining carbon compounds are very small concentrations of CH_4 and methane-related THC in the off-gas and acetic acid in the effluent, which is recycled as a nutrient to the PAC process, and the regenerated PAC.

Table 5 Wet air oxidation off-gas analysis

CO_2	13.46%
O_2	2.48
N_2	84.19%
CH_4	2.4 ppm
CO	<1%
THC	550 mg/L

This test was only a feasibility test with the operating parameters selected based on ZPI's experience. Plans to further evaluate the PACT and WAO processes for treating RDX manufacture wastewater using a 125 gpd mobile pilot plant on site at HSAAP have been dropped due to the demise of the RDX Expansion plant.

Another application of WAO, suggested by this author in 1989 and now being evaluated at the University of Maryland under funding from the U.S. Army Construction Engineering Research Laboratory, is the destruction of red water by WAO. (The complex composition of red water is shown in Table 6.) This would result in the oxidation of inorganic salts to their highest

TABLE 6
Radford AAP Red Water Solids

CHEMICAL	PERCENT
<u>INORGANIC SALTS</u>	
● SODIUM SULFITE	21.5
● SODIUM SULFATE	10.8
● SODIUM NITRITE	11.2
● SODIUM NITRATE	1.5
● SODIUM SULFIDE	MAY BE PRESENT
● SODIUM CARBONATE	MAY BE PRESENT
TOTAL	45.0
<u>ORGANIC NITROBODIES</u>	
● SODIUM SULFONATE OF 2,4,5-TNT	22.7
● SODIUM SULFONATE OF 2,3,4-TNT	9.6
● SODIUM SULFONATE OF 2,3,6-TNT	2.0
● SODIUM SULFONATE OF 2,3,5-TNT	TRACE
● ALPHA-TNT-SELLITE COMPLEX	16.2
● 2,4,6-TRINITROBENZOIC ACID SODIUM SALT	1.0
● WHITE COMPOUND SODIUM SALT	1.0
● TRINITROBENZALDEHYDE BISULFITE ADDITION COMPOUND	1.0
● TRINITROBENZYL ALCOHOL	1.0
● SODIUM NITROFORMATE	0.5
● 3,4-DINITROBENZOIC ACID SODIUM SALT	TRACE
● 2,3-DINITROBENZOIC ACID SODIUM SALT	TRACE
● TRINITROBENZENE-SELLITE COMPLEX	TRACE
● DISSOLVED 2,4-DNT	TRACE
● DISSOLVED m-TNT	TRACE
TOTAL	55.0

oxidation state, decomposition and oxidation of organic sodium salts and destruction of organic compounds. The resultant stream would consist of sodium sulfate, nitrate and hydroxide, plus residual organics. Unofficial



results, not yet published, indicate red water samples, diluted 100:1 to facilitate the test equipment, experienced a COD reduction from 700 mg/L to 10 mg/L and TOC reduction from 450 mg/L to 4 mg/L. This stream could then be further treated in a conventional biological treatment plant. The Army's Toxic and Hazardous Materials Agency, at its 14th Annual Army Environmental R&D Symposium in November 1989 rated the WAO technology as the most promising technology for treating red water. (Ref. 4)

If TNT in the plant effluent was a problem, two options are available. First, if the TNT containing streams could be isolated, they could be sent to the WAO unit for treatment. If not, the effluent could be treated in a PACT plant in conjunction with WAO. PACT treatment of TNT production wastewater (not red water) has already been successfully demonstrated on a bench scale by ZPI using pink water from the manufacture of TNT at Canadian Industries Limited (CIL). (Ref. 5)

APPLICATION TO POLLUTION ABATEMENT PROBLEMS AT RAAP

The following RAAP pollution abatement problems can be addressed by PACT or WAO technology, or a combination of both.

Wet Air Oxidation/Biological Destruction of NC Fines

Abatement of TNM in the Process Tail Gas from TNT Manufacture

Removal of Dinitrotoluene (DNT) from Propellant Wastewater

Destruction of Bioplant Sludge

Nitroglycerin (NG) Vapor Destruction

Biological Destruction of TNT Waste

Abatement of TNT Red Water

The destruction of both NC fines and bioplant sludge can be addressed by WAO treatment. The bioplant sludge is now classified as a hazardous waste (K044) and the NC fines have recently been re-classified as a hazardous waste, resulting in major disposal cost increases for RAAP. It is proposed to treat the bioplant sludge, a concentrated stream, and the NC fines, a dilute stream, both as mixtures and as discrete streams. Part of the effort is to be dedicated to concentration of the NC fines from approximately 70 mg/L at 3.4 MGD to a more effective treatment volume. One possible method of treatment would be to pass the NC fines stream, after some settling, through the bioplant. Although it is not anticipated that the NC fines would be affected by the biomass, the biomass should attach to the NC fines and aid in flocculating the NC fines, for ultimate destruction by WAO with the bioplant sludge. The treated WAO effluent would either be



subjected to biological treatment if necessary, or discharged from the plant directly.

The most serious obstacle to resumption of TNT production in this country is elimination or disposal of red water.

A temporary solution has been found, should large scale TNT production be resumed soon. This would allow shipment of the red water to Dupont's Chambers Works for treatment in their wastewater treatment plant (which is, by the way, a PACT plant). Long-term approaches being considered are replacing the toluene feed with purified orthonitrotoluene to minimize or eliminate red water generation, or improved incineration to destroy the red water generated.

Another long-term solution to this problem is the destruction of red water by wet air oxidation. In addition, enhanced biological destruction of TNT production wastewater would be evaluated on a pilot scale using the PACT process. The evaluation of PACT and WAO for the treatment of red water and other wastewater from TNT manufacture has been discussed in the previous section of this paper.

The same evaluation of CIL's TNT production wastewater also demonstrated removal of DNT, a known carcinogen and EPA priority toxic pollutant, down to non-detectable levels. DNT is found in RAAP's wastewater in concentrations of up to 6 mg/L, with only partial removal in the bi-plant, resulting in DNT being discharged to the New River. Renewed production of TNT, previously referred to, would result in additional DNT discharges. This DNT stream can be treated by the PACT process.

Solution of the remaining problems, TNM abatement and NG vapor destruction, is not as straight-forward and raises some questions. Both efforts involve adsorption of the vapor, either acetone-alcohol-NG or TNM, on PAC, either in the feed/recycle stream to the PACT unit or directly in the PACT unit. The idea is to affect adsorption on the PAC with inception of biodegradation, thus reducing the hazardous nature of the TNM or NG. Both substances, but especially the NG mix should be amenable to this type of treatment. However, primary emphasis should be placed on the NG problem. The TNM is a possible problem if TNT manufacture is resumed; the NG-acetone-alcohol problem is current and serious, as the release of VOC's to the atmosphere affects ozone formation. The Navy reports carbon can safely adsorb and decompose NG. Also, NG is apparently at least partially degraded by conventional biological treatment. Biodegradation of acetone and alcohol is no problem at all. Thus, once adsorbed into the PACT system, complete biodegradation is probable based on the synergistic effects of PAC and activated sludge.

Summary

The advantages and disadvantages of PACT and WAO are shown in Table 7.

TABLE 7 ***Advantages/Disadvantages for*** ***PACT/WAO Processes***

ADVANTAGES

- SYNERGYSTIC EFFECT OF PAC AND ACTIVATED SLUDGE TREATMENT SHOULD ENHANCE REMOVAL OF COD AND BOD, INCLUDING TRACE NITRAMINES
- WAO OPERATION
 - OXIDIZES THE SLUDGE, LEAVING A VERY SMALL AMOUNT OF ASH
 - REGENERATES THE CARBON, ELIMINATING A CARBON DISPOSAL PROBLEM
 - DESTROYS ABSORBED ORGANICS
 - OFF-GAS CONSISTS OF CO₂, N₂, AND LOW M.W. ORGANICS (FED BACK TO PACT UNIT AS CARBON SOURCE)
- CHANGE MODE OF ANOXIC FILTER FROM FIXED FILM TO SUSPENDED GROWTH, ELIMINATING COST OF, AND PROBLEMS RELATED TO, USE OF FILTER MEDIA
- ELIMINATES AEROBIC DIGESTER AND POST THICKENER
- ELIMINATE, DOWNSIZE OR MODIFY DEWATERING REQUIREMENT, DUE TO GREATLY REDUCED GENERATION OF SLUDGE
- REPLACE FeCl₃/LIME ADDITION WITH POLYMER
- EXPECTED COMPLETE REMOVAL OF EXPLOSIVES SHOULD ALLOW RECYCLE OF EFFLUENT
 - ELIMINATE REAERATION
 - MINIMIZE WATER TREATMENT PLANT OPERATIONS
- VOLATILE COMPONENTS ABSORBED, TREATED IN PACT; ODORS MINIMIZED

DISADVANTAGES

PACT

- ONE MORE PARAMETER TO CONTROL

WAO

- HIGH COST UNIT, USUALLY REQUIRES TITANIUM
- HIGH MAINTENANCE
 - MONTHLY SHUT-DOWNS FOR CLEANING
 - SPECIALIZED TITANIUM WELDING TECHNIQUES



The PACT and WAO processes, as a result of analysis of the process mechanisms, wide-spread commercial acceptance and application, and limited pilot testing and evaluation, appear to be highly capable of providing enhanced tertiary treatment of wastewaters generated by the manufacture of P&E, including red water. Conventional parameters of wastewater conditions, such as BOD, COD, TKN, TSS, NO_2 , etc. would be effectively addressed by these processes, as well as individual explosives and priority pollutants. In addition, the generation of sludge and hazardous waste (spent carbon) will be minimized or eliminated, as will be the discharge of toxic pollutants.

PACT is amenable to retrofitting an existing activated sludge plant since the process generally requires a smaller aeration basin. The generation of odors will be minimized or eliminated and the WAO emissions will be either nitrogen, carbon dioxide or be recycled to the PACT. Although the WAO is energy efficient, since the reaction generates enough heat to sustain the reaction and provide some heat for steam generation, the WAO unit is maintenance intensive as an inherent result of the reaction conditions. This is a factor that must be considered in all decisions to adopt PACT/WAO treatment.

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Progress in the Development of
Innovative Penetrometer Technology for
the Detection and Delineation of Contaminated Soil

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ABSTRACT

The Site Characterization and Analysis Penetrometer System (SCAPS) has been successfully deployed at four sites during last year. Experience with SCAPS has led to suggestions for improvements that can be incorporated into the next generation of SCAPS equipment. Improvements that are indicated include:

- a) Development of a downhole magnetometer to detect metallic obstacles ahead of the penetrometer.
- b) Incorporation of a robotic electronic surveying system to improve site mapping.
- c) Addition of a new solid state laser system to upgrade the soil fluorometer.
- d) Development of automated signature recognition techniques to allow quantification of compounds in complex mixtures.
- e) Development of a plasma emission system for screening for toxic metals in soil.
- f) Development of techniques for screening sites for explosives and solvent related wastes.
- g) Addition of a capability for on-site visualization of soil screening data.

SCAPS represents an evolving technology that will change with each new generation of equipment. The field evaluation program has been the most useful approach for producing proposed improvements.

INTRODUCTION

Background.-- The U. S. Army Toxic and Hazardous Materials Agency (USATHAMA) in cooperation with the USAE Waterways Experiment Station (WES) began work in 1986 on adapting cone penetrometer equipment for the investigation of hazardous waste sites. The program evolved into a Tri-Services Project involving particularly the Air Force Engineering and Services Laboratory and the Naval Ocean Systems Center (NOSC). The Environmental Protection Agency



has provided support for sensor development through the Environmental Monitoring Science Laboratory. The Department of Energy has now initiated participation in this program through the Office of Technology Development. The objective of the research and development activity has always been to produce equipment that can be used to screen sites for chemical or radiological contamination in a rapid and economical manner. The program has generated the first Site Characterization and Analysis Penetrometer System (SCAPS). SCAPS includes a suite of geophysical instruments for surveying the site for concealed obstacles and buried utility lines, a specially-designed truck (Fig. 1) housing the hydraulic rams for pushing the penetrometer rod, and a data acquisition and analysis system that can display sensor data on-site in real time. Laboratory-based computers are used to produce three-dimensional plots from completed site investigations. The SCAPS penetrometer currently has sensors that measures soil strength, electrical resistivity, and fluorescence of the soil immediately adjacent to the penetrometer rod. The SCAPS unit can also take soil and water samples and put monitoring instrument implants in place. Details on the capabilities of the current SCAPS unit are summarized in Table 1 and provided in detail in Lurk and others (1990) and Cooper and others (1989). The sequence of operation involved in a SCAPS investigation is presented in Fig. 2. The SCAPS unit is now over one year old and has been used at four field sites. With a background on SCAPS field operations it is now possible to suggest the course of future developments.

Purpose.--The purpose of this report is to discuss technical areas where the next generation of penetrometer equipment can be improved to provide better performance over a wider range of waste disposal sites. This report describes the research and development needs that have to be addressed to produce advanced screening tools needed in site characterization and remediation. The future research operations are outlined as needs perceived from field activities and steps designed to produce a new capability that addresses the need.



Fig. 1. Photo of the SCAPS penetrometer truck. The front compartment houses the hydraulic equipment for pushing the penetrometer rods. The rear compartment houses the instrumentation for soil screening.



TABLE 1

Technical Specifications for the
Site Characterization and Analysis Penetrometer System (SCAPS)

Geophysical Equipment

Magnetometer: Scintrex SC3
Electromagnetics: Geonics EM-31 and EM-38
Ground Probing Radar: GSSI Model 8

Location/Surveying Equipment

Laser Transit: Topcon EDM with data logger

Penetrometer Truck

Make: Modified M-814 Military Chassis, with all-wheel drive
Total Weight: 21,319 kg (47,000 lbs)
Power: 261 kw (350 hp) turbocharged Cummins Diesel
Length: 10.52 m (34.5 ft)
Width: 2.6 m (8.5 ft)
Height: 4.14 m (13.5 ft)
Van Body: Two compartments, each 2.29 m (7.5 ft) wide by 2.74 m
(9 ft) long by 2.13 m (7 ft) high, all stainless
steel skin inside and out
Auxiliary Equipment: PTO-driven hydraulic pump 56.88 l/min
(15 gpm) at 13.8 MPa (2000 psi)
PTO-driven 25 kw, 3-phase generator for
electrical power (110 v, 220 v)
Shock and vibration damped floor for
instrumentation compartment
Electronic governor for the main engine

Penetrometer Push System

Make: Hogentogler, Inc.
Rams: Twin hydraulic rams, with chuck, 122-cm (48-in.) stroke
Force Output: 177,930-N (40,000-lb) push, 266,890-N (60,000-lb)
retract at 13.8 MPa (2000 psi)
Speed: 2 cm/sec (regulated) during push, up to 12 cm/sec retract
Controls: Hydraulic manifold, manual lever valves, pressure
regulated, solenoid-operated emergency pressure
dump valve
Subframe: Heavy wall 20.3-cm (8-in.) square steel members
Leveling: Four hydraulic jacks, two each fore and aft of van
body

Grouting System

Make: WES-designed, through-the-rod grouting system
Capacity: Handles one- or two-component chemical grouts at 5.6 l/min
(1.5 gpm) at 13.8 MPa (2000 psi) with positive
displacement pumps

TABLE 1 (CONTINUED)

Sensor Systems

Soil Strength: WES-designed tip and sleeve strain-gage system
Electrical Resistivity: WES-designed, pulsed DC, Wenner-array,
5-cm depth of investigation
Soil Fluorometer: NOSC/WES-designed laser-induced, soil fluorescence unit,
Nitrogen-laser excitation (337.1 nm), EG&G Optical
Multichannel Analyser III

Data Acquisition/Processing

Signal Conditioning: WES-designed, 8 channel data handling unit
On-site Data Processing: Two Hewlett-Packard Vectra Computers,
produce plots and displays of soil strength
measurements and inferred soil type, and
electrical resistivity or soil fluorescence
Off-site Data Processing: Silicon Graphics 4D/380 UGX with a Tektronix
Color Printer

Samplers

Soil: Mostap Soil Sampler and Gouda Soil Sampler
Fluid: QED Inc. Hydropunch Groundwater Sampler



SCAPS OPERATION

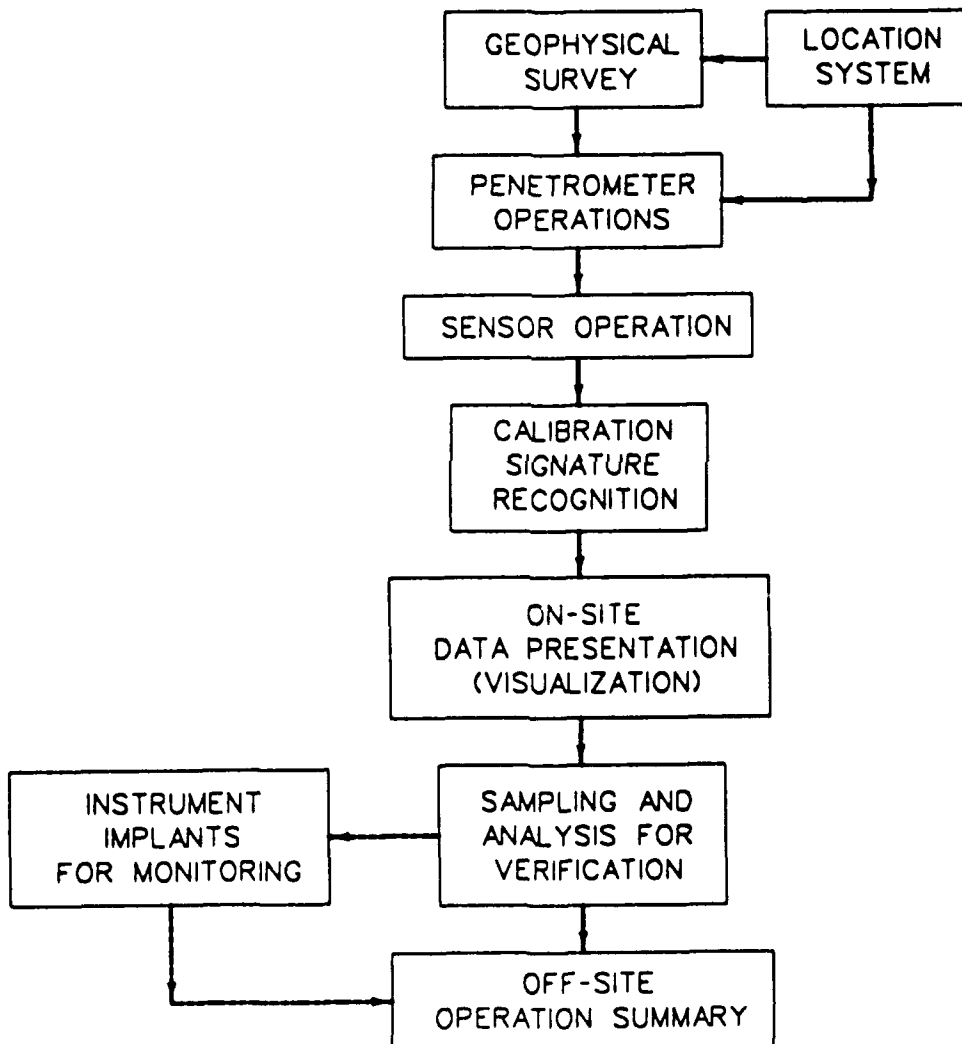


Fig. 2. Sequence of operations involved in a SCAPS site investigation.

GEOPHYSICAL SURVEYING

The use of the SCAPS system involves pushing a instrumented steel rod to a depth of approximately 50 meters into soil. Forces on the rod may exceed 75 MPa. Strain gauges are installed on both the rod and push frame that can measure the force on the tip of the rod and can indicate when the rod has encountered an impenetrable obstacle that can do harm to the instruments. The existing instrumentation on the rod cannot discriminate between a heavily cemented soil layer and a steel drum or an electrical conduit. The geophysical survey (scans with magnetometers, induced electro-magnetic equipment and ground penetrating radar) routinely conducted on the surface will warn of problems if the metal items (or buried utilities) are near the ground surface. Surface geophysical surveys are absolutely necessary but will never "see" as deeply as the penetrometer can be pushed.

A need exists for a geophysical sensing system that can go into the ground with the penetrometer rod to warn of obstacles ahead of the rod. The advanced geophysical survey capability may take the form of a magnetometer or electromagnetic unit built into the penetrometer rod. A penetrometer-based magnetometer or induced electromagnetic (E-M) is not available as a commercial tool but the model for the development is available in well logging equipment.

DETERMINATION OF THE LOCATION OF THE SENSOR

The SCAPS unit can complete a single push in less than 30 minutes and the sensors reading are typically made at approximately 2-cm depth intervals. The speed and precision of the truck operation puts new demands on the ability to determine the position of the penetrometer push sites and provide the map base for the field study. In current operations a survey crew is kept occupied by determining the coordinates (in three dimensions) for each penetrometer push location, in "shooting in" the surrounding cultural features and laying out the geophysical survey lines. All surveying is currently being done with an IR laser-based electronic distance measuring instrument (EDM) with a two- or three-man crew. As more dangerous sites are investigated the level of personal protective gear required will increase and site survey requirements will become a major obstacle to rapid operations.

A new position determination system is a definite requirement in the next generation of SCAPS tools. The new mapping system will have to be able to produce data with the precision of an EDM, but with much reduced manpower. At the present time, radio frequency and acoustical beacon systems cannot come close to the EDM in precision surveying (especially in determining elevation) and the satellite-based ground positioning systems cannot achieve the needed accuracy. The solution being explored currently is a robotic EDM that uses a servomechanism to direct a high-precision, IR laser-survey instrument on a target reflector (McCleave and Hart, 1989). Commercial robot surveying instruments are available now that can routinely determine range within 10 mm within a distance of 2000 m within 10 seconds time and are crewed with only one person. The position of the penetrometer relative to benchmarks on the site can become part of the real-time data available on the penetrometer display.



FLUOROMETRIC SENSORS FOR ORGANICS

The laser-excited, fiber optic fluorometer currently being used with the SCAPS penetrometer is described in detail in Lurk and others (1990). There are a number of design variations, but the newest systems uses UV-light (337 nm) from a pulsed nitrogen laser fired down an optical fiber and through a sapphire window in the wall of the penetrometer and into the soil. Light produced by fluorescence in the soil layer adjacent to the window is collected with a second fiber and passes up to an optical multi-channel analyzer in the instrumentation compartment in the truck. The nitrogen laser operates satisfactorily and can determine diesel fuel contamination at levels as low as 200 ppm. Replacing a gas laser with a solid state laser is advantageous because the modification will provide greater power (a 10-fold increase in energy) and shorter wavelength (more energetic) UV. The solid state laser does not require that flowing nitrogen be present in the lasing cavity. Using a solid state laser eliminates the need for handling compressed gas cylinders on the waste site.

A new fluorometer design being developed for SCAPS uses a multiply-doubled, pulsed Nd:YAG laser and provides two wavelengths (355 nm and 266 nm) in the UV for sample excitation. Upgrading the system with a more powerful, multifrequency excitation source has called for a redesign of the optical fiber link and for changes in the signal processing. The upgraded fluorometer will be capable of examining the time lag associated with excitation of the contaminated soil at two separate wavelengths. The increased power will reduce the need to stack signals to increase sensitivity (although the option to stack signals will always be available). All changes in the system are designed to increase the sensitivity and specificity while maintaining the standard soil penetration rate of 2 cm/sec.

SIGNATURE RECOGNITION

The SCAPS fluorometer has been largely used in the detection and delineation of fuel-contaminated soils. The character of the products detected was determined by examining the wavelength of maximum fluorescence and noting the position of the most prominent peak.

Enhancing the amount of data obtained from the fluorometer by using two excitation wavelengths makes it useful to develop an automatic signature recognition system for the specific organic contaminants or mixtures of contaminants. Plans are underway for developing a signature recognition approach for the determination of relative amounts of different components in complex mixtures of organics from the fluorescence spectra. Plans are being made to look at automated techniques involving principal component analysis and neural networks for interpretation of fluorescence spectra (Long, Gregoriou and Gemperline, 1990; Wythoff, Levine and Tomellini, 1990). Efforts at complex spectral analysis will be of great benefit as tunable lasers that can provide many more excitation frequencies become available.

PLASMA EMISSION ANALYSIS FOR METALS IN SOIL AND GROUND WATER

The SCAPS program has always had the development of a sensor system for measuring the concentration of metals in soil and groundwater as a goal. Pollution from toxic metals has been a continuing problem at some Army



installations especially where plating and paint stripping wastes were landfilled. At the present time there is no technique for rapidly screening soils for toxic metal contamination with the penetrometer.

National Aeronautics and Space Administration (NASA) has been supporting research on techniques for on-line chemical analysis of metals in plant growth media (hydroponic solutions). A novel fiber optic plasma emission system has been developed in the NASA program that uses a plasma created under water to produce the characteristic emission lines for metals (Schlager, 1990). The light gathered from the plasma is passed up a fiber optic link to an optical multichannel analyzer (Figure 3). The plasma emission system has not been fully optimized, but initial data indicate that most toxic metals will be detectable at levels sufficiently low for the emission system to be of use at contaminated sites.

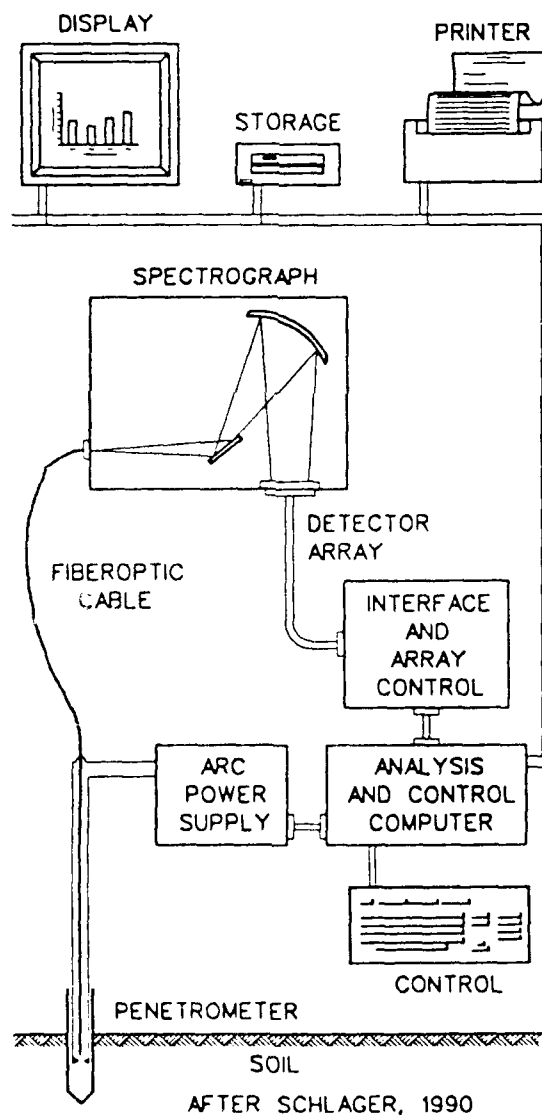


Fig. 3. Schematic diagram of the proposed plasma emission system for screening soil for potentially toxic metals.

DETECTION TECHNIQUES FOR SOLVENTS AND EXPLOSIVES

Solvents and explosives wastes are other major contaminants of concern in the SCAPS program. These wastes represent unusual problems in that they are often present at very low levels and detection of the specific compounds of interest may require modification of the operation of the penetrometer. The sensors may have to be left in place or moved slowly through the soil.

Work is underway on techniques for the using the penetrometer in screening for waste solvents and wastes from explosives manufacture at both NOSC and WES. Both of these wastes are complex mixtures of organics that include a wide variety of compounds in addition to the primary pollutant being tracked. While the primary pollutant may not have recognizable signatures when soil/waste spectra are examined, minor components may be more easily detected. For example, vapor degreaser sludge, a primary waste product containing trichloroethylene (TCE), also contains oil and grease and other solvents such as xylene that can be detected spectroscopically far more easily than pure TCE. The detectable compounds may act as "pathfinders" for pollutants that are harder to find and identify.

THREE-DIMENSIONAL VISUALIZATION OF PENETROMETER DATA

A cone penetrometer unit can push over 200 meters of holes in a single day (the equivalent of four 50-meter deep holes). A typical waste investigation in a fuel storage area may involve 20 to 30 holes. The fluorometric data in a site characterization operation alone could result in a spectrum recorded for every 2 centimeters of penetration. A site investigation can easily involve 10,000 fluorescence determinations. The high density of data points that the penetrometer can generate requires the use of scientific visualization as a data interpretation tool.

At the present time, SCAPS data is being reduced using the Interactive Volume Model (IVM) developed by Dynamic Graphics (Alameda, CA). IVM grids the data in three-dimensions using an implementation of a minimum tension gridding system (Briggs, 1974). The program searches for data points both by distance and angular position with regard to the grid node. Grid node estimates are first made on widely spaced nodes. A surface is fitted to the original grid using a biharmonic cubic spline function and the scattered data points are compared to the surface. The grid nodes are recalculated and refined. The three-stage operation establishes a general shape based on widely spaced nodes and then fills in local details.

Test runs are underway to develop techniques for optimizing the number of test holes and the positions of test holes to take advantage of the power of the gridding system while operating within the mobility or equipment access constraints at a hazardous waste site. On-site visualization can be made from a system for guiding the investigation that is in progress. Figures 4 and 5 show how the size and shape of a soil volume suspected of being contaminated will change as the density of the data points increases. Increasing the data density increases the detail that is added to the shape of the contaminated soil volume. The preliminary work that has been completed indicates that running the visualization program at different points in the data collection process can provide insight into the best locations for additional holes.

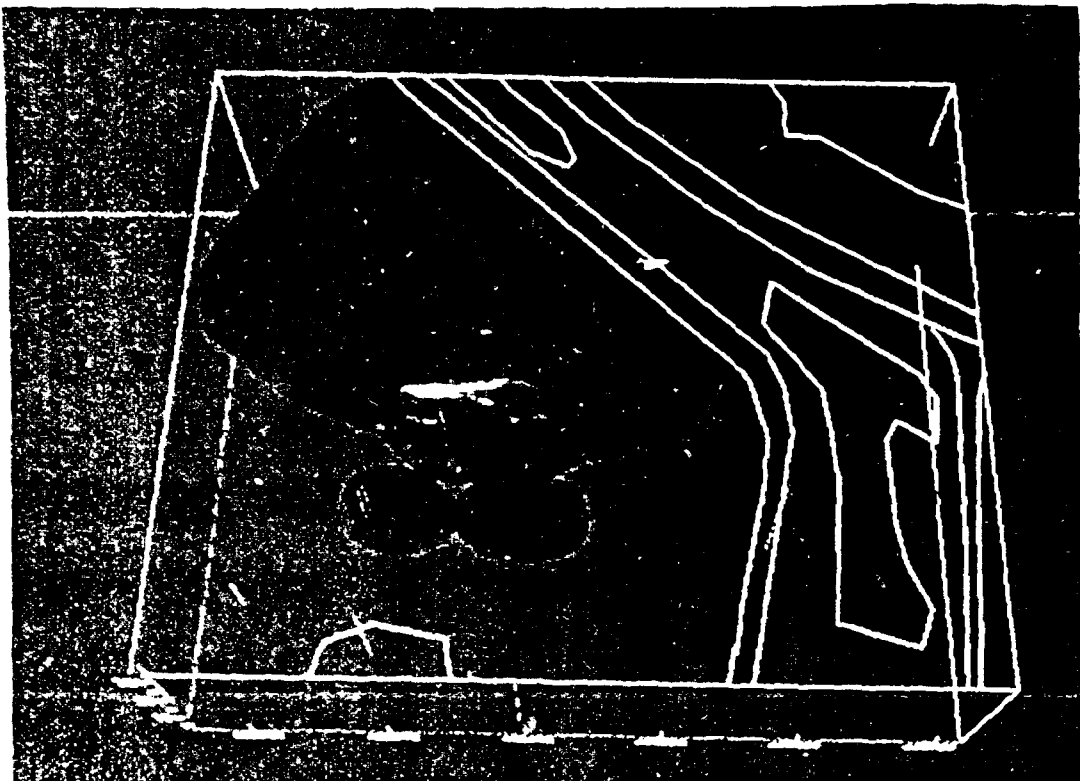


Fig. 1. A photograph of the object shown in Fig. 1, illuminated at an angle of 45°. The object is a rectangular block of material, possibly a book or a box, with a dark, textured surface. The image is grainy and has a high level of contrast.

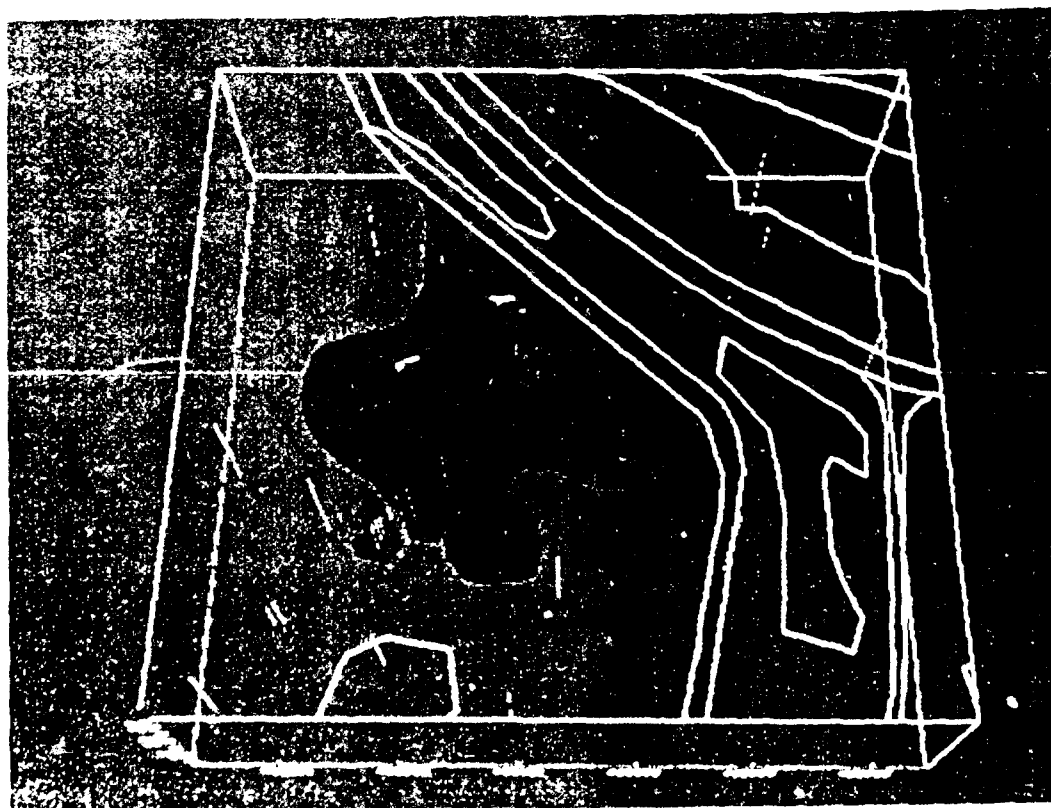


Fig. 2. A photograph of the object shown in Fig. 1, illuminated at an angle of 45°. The object is a rectangular block of material, possibly a book or a box, with a dark, textured surface. The image is grainy and has a high level of contrast.

CONCLUSIONS AND RECOMMENDATION

The first SCAPS unit successfully demonstrated that the penetrometer can be equipped with sensors and used to screen waste sites for contaminated soil. While the current equipment functions satisfactorily the following items are viewed as improvements to upgrade the existing SCAPS system:

- a) Development of a downhole magnetometer (or E-M) to locate metal items that can damage the penetrometer instruments or create a hazard for personnel on the surface.
- b) Integration of a robotic EDM unit to reduce the time and manpower needed for site surveys.
- c) Addition of more powerful solid state laser with two UV excitation frequencies to the soil fluorometer unit.
- d) Development of a plasma emission unit for the in-situ screening of soils for metal contamination.
- e) Development of automated signature recognition for the detection and quantification of pollutants in complex spectra.
- f) Development of techniques for using "pathfinder" compounds in screening for organic contaminants that are difficult to detect.
- g) Addition of a field workstation that will allow on-site visualization of the data collected over a site at different stages as the site characterization operation proceeds.

SCAPS is an evolving project and improvements in the hardware and data acquisition and processing will continue. The major input for modification and development of the equipment will probably come from the evaluation of field trials of the last generation of equipment.

ACKNOWLEDGEMENTS

The SCAPS is a Tri-Services Project that represents the combined efforts of large number of researchers. We extend our particular thanks to Mr. Gregory Theriault (NOSC) for work on the design of the new laser excitation system. Dr. Sabine Apitz (NOSC) suggested the useful approaches to signature recognition. Dr. Barry McCleave (WES) is responsible for suggesting the addition of the new surveying system. Dr. Kenneth Schlager (Biotronic Technologies, Inc.) is working on adapting the plasma emission system for use in the penetrometer. The project is under the direct supervision of Mr. Joseph R. Curro, Jr., Chief, Engineering Geophysics Branch, Dr. A. G. Franklin, Chief, Earthquake Engineering and Geosciences Division, Geotechnical Laboratory (WES) and Mr. Robert P. Bartell (USATHAMA).

The test described and the resulting data presented herein, unless otherwise noted, were obtained from the research conducted under the Site Characterization and Analysis Cone Penetrometer Program of the United States Army Corps of Engineers by the USAE Waterways Experiment Station. Permission was granted by the Chief of Engineers to publish this information.

The views of the authors do not purport to reflect the position of the Department of the Army or the Department of Defense. Citation of trade names does not constitute an official endorsement or approval of the use of any commercial product.



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RESULTS FROM THE SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION (SITE) DEMONSTRATION PROGRAM

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ABSTRACT

The need for long-term, permanent treatment solutions as alternatives to land disposal has been highlighted by legislation such as the Hazardous and Solid Waste Amendments of the Resource Conservation and Recovery Act (RCRA) and the Superfund Amendments and Reauthorization Act (SARA) of 1986. SARA directed the U.S. Environmental Protection Agency to establish an "Alternative or Innovative Treatment Technology Research and Demonstration Program" to identify promising waste treatment technologies, assist with their evaluation, and promote their use at Superfund sites. In response to this direction the Superfund Innovative Technology Evaluation (SITE) Program has evolved to provide documentation of engineering, performance, and cost information for innovative alternative technologies so that they are developed, evaluated, and made commercially available for the permanent cleanup of Superfund sites.⁽¹⁾ Demonstration projects identify limitations of the technology, applicable wastes and waste media, potential operating problems, and the approximate cost of applying the technology in the field. Twenty-one demonstrations have been completed to date with reports available for ten of them. Information from the most recently completed demonstrations, along with relevant activities at each site, are summarized. Projects described herein include the microfiltration work of DuPont and the Oberlin Filter Company, waste excavation and emissions control work sponsored by EPA Region 9, the AWD Technologies demonstration of integrated vapor extraction and steam vacuum stripping, solidification of contaminated soil by Silicate Technology Corporation, recovery of lead utilizing the flame reactor developed by Horsehead Resource Development Company, and evaluation of the ongoing cleanup effort of SoilTech with the anaerobic thermal processor.^{(2) (3)}

INTRODUCTION

The goal of the SITE Program is to ensure, to the greatest extent possible, that innovative/alternative technologies are developed, demonstrated, and made commercially available for the permanent restoration of Superfund sites. Through the Program, the Agency strives to provide accurate and reliable performance, engineering, and cost data on these technologies to potential users. The Demonstration and Emerging Technologies Programs are responsible for waste treatment technology development, while separate activities are promoting the development and evaluation of measurement and monitoring technologies as well as technology transfer operations.

The Emerging Technologies Program provides a framework for encouraging and testing pilot-scale technologies that have been proven at bench-scale but are not ready for field evaluation. Under this Program, EPA provides funding to developers through a competitive cooperative agreement process to support pilot-scale process development and testing. Cost sharing by the technology

developer is an important aspect of the cooperative agreement which is intended to foster the commercialization of additional technologies having application to the cleanup of hazardous waste sites.

Sixty-six projects are now part of the Demonstration Program where technology developers and EPA participate in joint ventures to operate and evaluate cleanup processes. Primary benefits of the Program for developers include: experience gained from operating the process at a Superfund site; acquisition of valuable regulatory background; increased public awareness of the technology and its capabilities; and documentation of the applicability of the process to remediation of hazardous waste sites. In general, the developer is required to operate the technology at a selected location. EPA is primarily responsible for development of a demonstration plan, sampling and analytical operations, reporting, and technology transfer activities. Demonstrations at Federal or State Superfund sites (remedial or removal action sites), EPA test facilities, or at Federally owned sites are encouraged; however, if such sites are neither available or applicable, a developer's facility or a private site may be utilized. EPA is becoming increasingly flexible in the designation of appropriate sites as the Demonstration Program continues to evolve.

DEMONSTRATION PROGRAM

Technologies selected to participate in the Demonstration Program must be either in the final stages of field-scale development with available hardware, or fully developed with all equipment constructed and ready for use in the field. Emphasis is placed on innovative/alternative technologies that have been developed to the extent that a demonstration will enhance the application and commercialization of the process. The technology demonstration provides data to potential users to aid them in making decisions on the applicability of the technology for a specific site.

The scale of a demonstration is flexible in order to accommodate the wide variety of technologies that enter the program. Criteria for determining the size and length of a demonstration are based on quality control, cost, and scale-up considerations.

As noted above, technology demonstrations may be conducted at Federal or State Superfund sites (remedial or removal action sites), EPA Test and Evaluation (T&E) facilities, federally owned sites, private sites, or the Developer's facility. Generally, Superfund sites do not require permits; however, if necessary, EPA will assist a developer in acquiring permits or in meeting the substantial requirements of a permit for a demonstration conducted at a Superfund site or a Federally owned facility. All required permits should be obtained by the developer and be in place prior to the selection of any other location for a demonstration. Selection of a site is undertaken by the SITE Program in conjunction with the developer, EPA's Office of Solid Waste and Emergency Response (OSWER), and EPA's Regional Offices.

While selection of a site is primarily EPA's responsibility, developers are encouraged to recommend potential sites that are applicable to their technologies. A site visit by the EPA Project Manager and the developer, for the purpose of determining if a site is appropriate, is one of the first actions of a demonstration. EPA also assigns a support contractor to the

demonstration to assist with and/or conduct all aspects of the technology evaluation under the direction of the EPA Project Manager.

A technology demonstration is a mutual arrangement and neither EPA nor the developer may proceed without agreement from the other party. Where site selection, operations planning, or time schedules cannot be mutually arranged, EPA may cancel the demonstration or a developer may choose to exit the Program without penalty.

PRODUCTS OF THE DEMONSTRATION

The final products of each demonstration project will typically be two EPA reports; a Technology Evaluation Report (TER) and an Applications Analysis Report (AAR). The TER documents the results of the technology performance. It includes a rationale, description of the technology, and operations plan, sampling and analysis procedures, health and safety issues, test results with associated QA/QC data, and cost data. This lengthy and detailed presentation is prepared by EPA, reviewed and approved by the developer, and distributed through the National Technical Information Service (NTIS). A project summary covering this same material is printed and distributed by EPA.

The Applications Analysis Report discusses the applicability of the technology to other waste media, sites, constituents and concentrations, as well as a definition of the capital and operating costs. EPA is utilizing a common format in presenting cost information for all final SITE reports. These costs shall include but not be limited to the following items: operating cost; maintenance cost; waste pre-treatment and post-treatment costs (if applicable); and the potential for cost recovery (ability to recycle residues or process streams). A special section of this report is also dedicated to the developer for comments, concerns, or additional technology claims. This "Vendor Claims Section" appears unedited in each AAR.

Although EPA works with the developer throughout the demonstration process, including publication of the final reports, EPA maintains editorial control over the contents of the reports produced at the conclusion of the project, with the exception of the developer claims section of the AAR. Furthermore, the Agency conducts an independent evaluation of the developer's claims and will support claims made about the technology only to the extent that they are clearly proven by the data obtained during the demonstration or other reliable and available data.

To supplement the above EPA reports, demonstration results are also presented at technical conferences and/or published as technical papers in journals and proceedings. These reports and papers provide EPA, States, industry, and the public with performance data on new commercial technologies, and with specific cost data useful for comparing and selecting on-site cleanup technologies. Endorsements, approvals, or certifications of a technology, however, cannot be provided by EPA. Other technology transfer items coming from a demonstration include the widely-distributed, two-page demonstration bulletin and a short video-tape presentation of the demonstration and its results.

RECENTLY COMPLETED DEMONSTRATIONS

Membrane Microfiltration

E.I. DuPont de Nemours & Company, Inc. and the Oberlin Filter Company demonstrated a microfiltration technology for removal of suspended solids from wastewater at the Palmerton Zinc Superfund Site, Palmerton, PA, in April 1990. The project was undertaken to evaluate the ability of the technology to remove zinc (Zn) and total suspended solids (TSS) from the site's shallow groundwater. Pretreatment of the groundwater to precipitate dissolved Zn and other metals was included as part of the demonstration program. The microfiltration system utilized DuPont's Tyvek T-980 membrane filter media in conjunction with the Oberlin automatic pressure filter. During optimum operating conditions the system removed both Zn and TSS at a rate of 99.95%. The filtrate met applicable National Pollutant Discharge Elimination System (NPDES) permit limits for discharge to a local waterway for metals and TSS, (maximum daily discharge limits to Aquashicola Creek for Zn and TSS are 2.4 and 30 mg/l, respectively). The filter cake resulting from the process passed the paint filter liquids test for free liquids at all operating conditions. A composite cake sample for the total demonstration successfully passed both the Extraction Procedure (EP) Toxicity and Toxicity Characteristics Leaching Procedure (TCLP) tests.

Excavation Techniques and Foam Suppression Methods

A trial excavation of approximately 137 cubic yards of waste, sponsored by EPA Region 9, was performed at the McColl Superfund Site, Fullerton, CA, during July 1990. Objectives of the demonstration were to better determine the nature of this waste and the treatment needed to improve its handling characteristics, to measure the extent of air emissions that might occur during excavation, to assess emissions control provided by the enclosure and exhaust treatment system, to monitor emissions at the site boundary, to study the effect of vapor suppression foam during excavation activities, and to determine potential problems that might occur during excavation for full-scale remediation. The trial excavation was conducted within a temporary enclosure with air exhausted from the enclosure through a sodium hydroxide-based wet scrubber and activated carbon bed adsorber to reduce emissions of sulfur dioxide and organic compounds. Foam was used in an attempt to reduce atmospheric releases from the raw waste during excavation, processing, and storage activities. Waste at the McColl Site consisted of layers of overburden, mud, tar, and char from oil refining operations. The demonstration indicated that excavation is feasible under an enclosure, emissions from an enclosed site can be treated effectively with no adverse impacts at the site boundary, and the waste can be easily treated for further processing. Vapor suppressing foams did not appear to substantially reduce emissions from excavated material.

Integrated Vapor Extraction and Steam Vacuum Stripping

During September 1990, AWD Technologies, Inc. demonstrated its automated treatment unit, the AwaDator/SVF system, on volatile organic compounds (VOCs) at a Lockheed Aeronautical Systems facility in Burbank, CA. The AWD system has been on site for nearly two years to assist in remediation of the San Fernando Valley Superfund Site. The process combines a vacuum assisted steam

stripping tower (the AquaDetox unit) with a closed-loop soil vapor extraction (SVE) unit. Within the AquaDetox unit, organics are stripped from the groundwater, condensed, and collected for recycling. The tower operates under a moderate vacuum as steam is injected at the bottom. The SVE unit removes contaminated soil-gases from the vadose zone through a network of extraction wells. These soil-gases are then passed through two separate granular activated carbon (GAC) beds for hydrocarbon removal and reinjected into the ground. At the time of testing, the AquaDetox/SVE system was treating groundwater contaminated with as much as 2,200 parts per billion (ppb) of trichloroethylene (TCE) and 12,000 ppb of tetrachloroethylene (PCE). Soil-gas that was treated contained total VOC concentrations of 450,000 ppb. Preliminary results indicate that groundwater contaminants are reduced to virtually non-detectable levels, and soil-gas contaminants are reduced to about 350 ppb. Groundwater is being treated at a rate of 1,000 gallons per minute. Soil-gas is treated at a rate of 200 cubic feet per minute.

Solidification/Stabilization with Silicate Compounds

The Silicate Technology Corporation (STC) waste solidification and stabilization technology was demonstrated at the Selma Pressure Treating Site, Selma, CA, during November 1990. Principal contaminants in the soil at this wood treating site were arsenic, chromium, copper, and pentachlorophenol (PCP). The technology involved application of two groups of reagents: one for stabilizing organic contaminants and the other for inorganic materials. Both groups stabilized soil/waste mixtures by reactions involving alumino-silicate compounds along with other treatment chemicals. Products from each process group were then solidified. Preliminary results indicate that arsenic in the form of leachate from the stabilized waste, as measured by the TCLP, was reduced by up to 93% from the raw waste. A total waste analysis for PCP showed it to be reduced in the treated soil blocks by up to 98%.

Flame Reactor Process

The flame reactor process, operated by the Minerals and Resources Recovery Division of Horsehead Resource Development Company, Inc. (HRD), was demonstrated at an HRD plant site in Monaca, PA, during March 1991. Waste material treated by the unit was secondary lead smelter blast furnace slag. The HRD flame reactor process was designed to produce a recyclable heavy metal-enriched oxide product and a nonleachable vitrified slag from a variety of metal-containing waste feeds. The high temperature reactor contacts wastes with a very hot reducing gas for less than one-half second. Feed streams may include granular solids, soils, flue dust, slag, and sludge. Volatile metals in the feed are fumed and then captured downstream while nonvolatile metals are encapsulated in the vitrified slag. Objectives of the demonstration were to produce a metal oxide and nonleachable slag, evaluate the technology's reliability, and generate operating costs for future decision-making. The unit performed well during the three days of test runs. Performance data will be available by Summer 1991.

Anaerobic Thermal Processor

The anaerobic thermal processor (AIP), developed by Alberta Oil Sands Technology and Research Authority (AOSTRA), was demonstrated at the Wide Beach Development Superfund site in Brant, NY during May 1991. The technology

demonstration was accomplished as part of the full-scale remediation of the site by SolTech, a licensee of AOSTRA. The ATP system thermally desorbs organics such as polychlorinated biphenyls (PCB) from soil, and also provides for chemical dehalogenation of chlorinated compounds by addition of alkaline and polyethylene glycol reagents. In the process contaminated soil, sludge, and liquids are sprayed with the dehalogenation reagents and then transported through a unique rotary kiln divided into four discrete process zones. The demonstration was undertaken to assess the ability of the ATP to remove PCBs and other organics from soil, determine if dioxins or furans are produced in the system, determine operating conditions for the ATP, and assess operating and capital costs for the unit. During the demonstration three eight-hour runs were sampled extensively to provide the necessary data for evaluating the system. Initial results from this work should be available by Fall 1991.

FUTURE DIRECTION

During January of each year a new solicitation for projects, advertised in the *Commerce Business Daily*, is undertaken in order to identify new processes to be added to the Program. Developer proposals in response to this solicitation are evaluated by EPA for selection into the SITE Demonstration Program by mid-summer. Additionally, a small number of unsolicited proposals are received and evaluated throughout the year. Developers who have already arranged with an EPA Regional Office or a private client for a treatability study or field demonstration are good candidates for acceptance into the Demonstration Program in that many site selection and preliminary planning steps may be bypassed. Projects such as this are usually referred to as "fast-track" projects, where all attempts are made to fit the demonstration into the existing schedule that has already been developed independently.

Another major source for demonstration projects which has recently become available is the Emerging Technologies Program. As technologies move through this two-year program, with funding support from EPA, it is hoped that they will develop into field-ready processes for demonstration and evaluation. Three emerging technology processes have already been accepted for participation in a demonstration, and it is anticipated that this number will grow substantially in the near future.

As the SITE Program has matured over the past five years, it is increasingly apparent that a tremendous amount of flexibility is necessary in order to respond to the mandate of increasing this country's base of viable cleanup technologies. Encouraging fast-track projects, combining demonstrations with ongoing Superfund remediation or removal efforts, and cooperating with other agencies such as the Department of Defense and the Department of Energy is helping to increase the number and scope of demonstrations being undertaken. By October 1991 EPA hopes to have brought at least forty technologies to field evaluation.

While the Agency's demonstration experience grows, its needs are becoming more clearly defined. Although wastewater treatment will continue to be represented in the SITE Program, greater emphasis is being placed on source control of contaminants. Soil and sediment treatment, both on site and *in situ*, are of primary interest. Furthermore, EPA plans to concentrate some demonstration efforts on problem sites, and future solicitations may contain requests for processes applicable to remediation of specific types of sites.



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A PROGRAM FOR EVALUATION OF EMERGING TECHNOLOGIES TO TREAT SITE-SPECIFIC AND CHEMICAL-SPECIFIC WASTES AT THE ROCKY MOUNTAIN ARSENAL, COMMERCE CITY, COLORADO

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ABSTRACT

A major programmatic challenge in the remediation of contamination of large U.S. Department of Defense (DOD) facilities is the acquisition of reliable engineering and cost data to support the selection of alternative treatment technologies for potential inclusion in recommended site remedies. At the Rocky Mountain Arsenal (RMA) Superfund Site, Commerce City, Colorado, the U.S. Department of the Army's (Army's) environmental managers and their consultants recognized that the site-specific and chemical-specific problems at RMA necessitated the acquisition of treatability data for decision making. The needed data included information regarding the potential and cost for application of (1) new technologies to clean up contaminated media at RMA and (2) existing technologies in addressing the combination of contaminants and matrices unique to RMA. Also, throughout the remedial investigation (RI) and initial phases of the ongoing feasibility study (FS), the Army and its consultants were regularly approached

by technology developers in the private sector with potentially applicable technologies for cleanup at RMA. These factors led to the initiation of an Emerging Technology Evaluation Program (ETEP) at RMA, which provides a formal mechanism for evaluating proposals from the private sector for technology demonstration at RMA, with the potential for the conduct of joint treatability studies on RMA waste materials between the private sector and the Army.

BACKGROUND

The RMA Superfund Site is a former defense/industrial complex located in Commerce City, Colorado, approximately 10 miles northeast of downtown Denver. The Program Manager for RMA (PMRMA) has been tasked by the Army to mitigate contamination problems at RMA. Remediation programs are currently being conducted at RMA in accordance with a Federal Facility Agreement pursuant to the Comprehensive Environmental Response, Compensation and Liability Act (as amended by the Super-

fund Amendments and Reauthorization Act). Contaminants of concern at RMA include pesticides, warfare chemical agents, solvents, and process intermediates. Recently, during the FS program, it became apparent that the efficiency of remediation of site- and chemical-specific problems at RMA would be enhanced through the acquisition of reliable engineering and cost data regarding the selection of alternative treatment technologies, that could then be considered in addition to existing data on proven remediation methods, for potential inclusion in the recommended site remedy(s). Consequently, ETEP was designed. Harding Lawson Associates (HLA) was retained by the Army as the Army's consultant for ETEP and to provide technical support.

PROGRAM DESIGN

Elements of the program design phase for ETEP included (1) planning activities, (2) identification of FS data needs, and (3) preparation of a solicitation for technology demonstration.

PLANNING ACTIVITIES

During the initial phases of program design, it was decided by PMRMA that ETEP should be modeled after the U.S. Environmental Protection Agency's (EPA's) Superfund Innovative Technology Evaluation (SITE) program, which serves to facilitate the development and implementation of innovative treatment technologies for hazardous waste remediation on a nationwide scale. Accordingly, to gain perspective for proper program design, PMRMA and HLA conducted the following planning activities:

- Met with representatives of the EPA's Superfund Innovative Technology Evaluation (SITE) program
- Acquired and evaluated information from EPA's SITE program
- Visited the vendor of a representative operating technology accepted for demonstration in the SITE program

PMRMA and HLA representatives met with EPA representatives in February 1990 to discuss procedures and results of EPA's SITE

program. At this meeting, PMRMA acquired pertinent information from EPA not offered through standard SITE publications, such as (1) EPA's mailing list for solicitation of proposals, (2) outlines of representative technology demonstration plans, (3) proposal evaluation criteria and procedures, and (4) experience and advice from EPA SITE project managers regarding technology demonstration implementation and evaluation.

During the planning phase, PMRMA and HLA acquired and evaluated publicly available information regarding emerging and innovative technologies from EPA's SITE program, as well as from other public and private sector sources. PMRMA and HLA (1) received all EPA SITE publications, (2) accessed treatability data bases, including EPA's Risk Reduction Engineering Laboratory (RREL) and EPA's Alternate Treatment Technology Information Center (ATTIC), and (3) attended conferences/seminars.

To gain information regarding techniques for technology demonstration and evaluation, PMRMA and HLA representatives visited an operating SITE program technology demonstration. This visit to a zero emission groundwater treatment facility in Burbank, California, provided perspective regarding the following:

- Process sampling and evaluation methods
- Variables affecting process performance
- Technical, legal, political, and logistical problems encountered during startup and operation

As a result of these planning activities, PMRMA and HLA gained information necessary to structure ETEP similarly to EPA's SITE program.

IDENTIFICATION OF FEASIBILITY STUDY DATA NEEDS

At the time of the design of ETEP, the following list of site-wide contaminants of concern had been identified as the result of the



endangerment assessment (EA) during the RI, :

- Aldrin
- Arsenic
- Carbon tetrachloride
- Chlordane
- Chloroform
- Dibromochloropropane (DBCP)
- Isodrin
- 2,2-bis(para-chlorophenyl)-1,1-di-chloroethane (DDE)
- 2,2-bis(para-chlorophenyl)-1,1-tri-chloroethane (DDT)
- Dieldrin
- Endrin
- Fluoroacetic acid
- Hexachlorocyclopentadiene
- Mercury
- 1,1,2,2-Tetrachloroethane
- Tetrachloroethylene

The distributions and concentrations of these and other contaminants at RMA were such that the following specific problem areas were identified as priorities to be addressed under ETEP:

- Treatment of large volumes of soil containing relatively low concentrations of contaminants
- Biological technologies for soil and sludge that are capable of treating organic contamination, such as pesticides and hydrocarbon products
- In-situ treatment processes for soil/solids that affect groundwater contamination and provide alternatives to long-term conventional pump-and treat approaches to contamination cleanup
- Combinations of unit operations to create treatment trains for specific wastes
- Recovery of free product (e.g., benzene) from soil and groundwater

To allow for comparable evaluation of proposals and to establish an appropriate level for testing (i.e., bench scale versus pilot scale), technologies were categorized according to their level of development, as follows:

- Available Alternative Technology - Alternative technologies for which sufficient data from pilot-scale testing on hazardous wastes exists to allow prediction of the performance of a full-scale process on RMA wastes.
- Innovative Alternative Technology - Innovative alternative technologies for which sufficient data from bench-scale testing on hazardous wastes exists to allow prediction of the performance of a pilot-scale process on RMA wastes.
- Emerging Alternative Technology - Emerging alternative technologies for which insufficient data from bench-scale testing on hazardous wastes exists to allow prediction of the performance of a technology at a pilot-scale to treat RMA wastes.

SOLICITATION DESIGN AND PREPARATION

PMRMA and the U.S. Army Procurement Directorate (Edgewood), Aberdeen Proving Ground, Maryland (Army Procurement), prepared the solicitation for technology demonstration in late 1989 and early 1990. A Broad Agency Announcement (BAA) was selected as the mechanism for solicitation on the basis of the specific objectives and organization of ETEP. In contrast to a formal Request for Proposal (RFP), the BAA allowed the Army flexibility to (1) solicit for several different topical areas and (2) negotiate a "gift agreement" with prospective developers whereby no exchange of funding would occur.

The solicitation that resulted reflected the Army's intent to negotiate an agreement with each selected developer whereby the developer would bear the cost of any mobilization, test plan and health and safety plan preparation, and operation of the technology demonstration and the Army would provide chemical analyses and an evaluation report. Furthermore, the BAA reflected the Army's intent to be responsible for identification of an appropriate location for onsite testing, performing limited site preparation, conducting sampling and analysis activities, providing support in obtaining any necessary

permits, coordinating the demonstration with appropriate regulatory agencies (when necessary), evaluating and reporting upon the technologies, and presenting the process and results at various symposia. It was clearly stated in the BAA that the receipt and review of such proposals by the Army was entirely for the purposes of technical evaluation and in no way constituted an agreement to enter into any contractual or other relationship with prospective developers.

SOLICITATION PROCESS

PMRMA and Army Procurement prepared the solicitation for technology demonstration in late 1989 to address identified program objectives. A notice of availability of a BAA was published in the January 2, 1990, Commerce Business Daily, which indicated that the purpose of the program was to:

"provide an opportunity for Developers to demonstrate the performance of their technologies on RMA waste materials and to provide reliable and accurate information for the detailed analysis and selection of alternatives for RMA."

Technology developers were provided an opportunity to request, in writing, a copy of the BAA. Ninety-one developers requested copies of the BAA in advance of its distribution in mid-February 1990.

In March 1990, a preproposal meeting was held at RMA to familiarize prospective developers with RMA. At this meeting, highlights of the findings of the RI and details regarding ETEP and the solicitation were presented. Developers were provided an opportunity to submit written questions at the meeting, and written responses were subsequently provided. Questions asked by developers focused on the following:

- Number of technologies to be selected and level of Army funding for sampling and analytical work for each test
- Interpretation of the categorization of technologies (i.e., emerging, innovative, or available)

- Level of detail to be included in health and safety and quality assurance/quality control (QA/QC) submittals
- Schedule
- Alternatives to ETEP for submittal of proposals to the Army

A total of 14 proposals were received by the mid-April 1990 deadline for submittal of proposals under the BAA. General technology types included the following:

- High-energy electron irradiation treatment of water
- Electrocoagulation treatment of trace metals in water
- Foam extraction of organochlorine pesticides from structures
- Abrasive blasting for removal of contaminants from structural elements
- Low-temperature volatilization of soil, with scrubbing of the gas stream
- Soil vapor extraction, groundwater contaminant phase transfer, carbon treatment, and onsite thermal carbon regeneration
- Transformation of organic compounds in the aqueous phase to elemental carbon in the presence of heat and reactants
- Supercritical oxidation of water
- Recovery of nonaqueous-phase liquids
- Two-stage incineration in a fluidized bed reactor
- Solidification/stabilization by chemical treatment
- In-situ bioremediation
- Oxidation of materials in an aqueous phase at elevated temperatures and pressures
- Ex-situ biotreatment with the addition of powdered activated carbon



PROPOSAL EVALUATION PROCESS

The proposal evaluation process for ETEP consisted of (1) formation of a multidisciplinary evaluation panel, (2) development of proposal evaluation procedures and criteria, and (3) the evaluation process itself.

EVALUATION PANEL

PMRMA organized a multidisciplinary evaluation panel consisting of representatives of multiple organizations to review the proposals and provide evaluation results to PMRMA. Ultimate selection of technologies for demonstration was made by the Army. The panel consisted of representatives of PMRMA, Shell Chemical (another potentially responsible party at RMA), the Army's FS consultant, the Army's consultant for ETEP (HLA), and EPA.

EVALUATION CRITERIA

Proposals were evaluated on the basis of three criteria:

1. Technical merit
2. Applicability to RMA
3. Developer capabilities

Technical merit was evaluated on the basis of information requested in the BAA. This included a detailed description of the technology to be demonstrated, including objectives, approaches, methods. The relationship of the technology to the state of knowledge in the field and to comparable work in progress elsewhere was also evaluated, together with a bibliography and a list of pertinent literature citations. Specific points evaluated were as follows:

- Identification and significance of the treatment problem
- Technical objective
- Hypothesis (including the hypothesis to be tested and expectations and use of resulting data)

- Proposed demonstration plan, which consisted of an Operation Test Plan, a Health and Safety Plan, and a QA/QC Plan
- Background, including the basis for the study and previous related work
- Methods, including details regarding experimental design
- Estimates of the immediate and/or long-range usefulness of the technology

With regard to applicability of the technologies to RMA, the proposals were evaluated for their likelihood of success in solving treatability problems at RMA. The BAA identified the FS data needs and stated that "Each proposed technology must be a process that will address problems at RMA." In a cover sheet, developers were required to list the contaminants that the technology would treat and a hypothesis regarding how the technology would address an RMA problem area.

Capabilities of developers were judged largely on the basis of key personnel identified by the developer who would be involved in the effort. The qualifications of the principal investigator and the amount of time that he/she and other senior professional personnel would devote to the research were assessed. Facilities available for performance of the proposed technology were also evaluated.

Proposals were evaluated at two levels. Level 1 was designed to (1) remove from further consideration proposals that were obviously inapplicable, infeasible, or had a poor probability of success on the basis of both the technology involved and the developer's capabilities and (2) identify the need for additional information relative to proposals judged to be promising, for a more detailed Level 2 evaluation.

Following receipt of additional information regarding promising proposals, the Level 2 evaluation was performed. Level 2 evaluation consisted of a more detailed review of the technical merit of the proposal, applicability to RMA, and developer capabilities. For example, this more detailed review



included verification of the developer's calculations regarding volumes of sidestream wastes to be generated, and assessment of the validity of hypothesized treatment efficiencies, given the synergistic effects of complex waste streams at RMA.

EVALUATION RESULTS

According to the evaluation criteria discussed above, the evaluation process focused on a review of the proposals for technical merit, applicability to RMA, and developer capabilities.

Each organization on the review panel reviewed the proposals during the Level 1 evaluation process and each scored the proposals as "Pass," "Fail," or "More Information Required." Following this step, the panel met to reach consensus on the proposal scores. The panel collectively assigned a score of "Fail" to six proposals and a score of "More Information Required" to the remaining eight proposals. Developers of proposals scored as "More Information Required" were provided with a written request for more information and informed of the deadline for receipt of their response.

Following receipt of additional information, each organization on the review panel conducted a Level 2 evaluation of the proposals and the panel convened to reach consensus on the final scoring of proposals. Of the eight remaining proposals, four were assigned a score of "Pass" and four were assigned a score of "Fail" by the panel. The four proposed demonstrations judged by the panel as having technical merit and applicability to RMA, as well as adequate developer capabilities, were the following:

- High-energy electron irradiation treatment of water
- Electrocoagulation treatment of trace metals in water
- Foam extraction of organochlorine pesticides from structures
- Soil vapor extraction, groundwater contaminant phase transfer, carbon treatment, and onsite thermal carbon regeneration

Results of the panel review were communicated to PMRMA in June 1990.

TECHNOLOGY SELECTION

PMRMA was advised of the proposal scores assigned by the panel, but elected not to proceed further to test the four technologies recommended by the panel for demonstration at RMA because of the need to evaluate and test specific innovative and demonstrated technologies identified as "Representative Process Options" in the FS. PMRMA is currently developing the specific mechanisms for implementing this new programmatic direction.

The four proposals that passed the panel evaluation were referred to EPA for possible future consideration for demonstration in the SITE program.

CONCLUSIONS

The 1989 ETEP solicitation process constituted valuable experience for the Army in the solicitation and evaluation of proposals for waste treatment technology demonstration. The process provided a fair and equitable mechanism for each developer with a potentially applicable technology to set forth its proposal for consideration. PMRMA believes that the process conveyed a positive and proactive image regarding its commitment to use all means available to remediate RMA contamination and thereby protect human health and the environment.

A relatively small number of responsive proposals were submitted, in comparison to the number of developers of emerging, innovative, and available technologies. Subsequent interviews with developers that did not submit in response to the ETEP solicitation indicated that the large financial commitment necessary for the developer to mobilize and test its technology discouraged developers from responding. PMRMA and HLA concluded that if funds had been made available to developers to offset such costs, the response to the ETEP solicitation would have been much greater.

It is PMRMA's and HLA's opinion that the multiorganizational panel review of proposals



was a positive consensus-building process that resulted in fair and objective scoring.

RECOMMENDATIONS

At federal facilities conducting large environmental restoration programs, the responsible agency should consider the solicitation and evaluation of proposals from the private sector for waste treatment technology demonstrations. At RMA, the process provided an opportunity for all developers to set forth their proposals for consideration and conveyed a positive and proactive image of the Army's environmental program at RMA.

If solicitation for technologies is contemplated, it may be advisable to defer such activity until initial formulation of the clean-up strategy(s) has occurred (e.g., representative process options have been identified). Following this initial formulation of strategy, it may be cost-effective to solicit for targeted technology categories for which treatability data needs have been identified. For example, if ex-situ biological treatment is identified as a retained option for groundwater treatment, a targeted solicitation could be issued for this technology type.

To obtain proposals from a representative number of firms, funding of portions of the mobilization and/or testing of the technology is recommended, especially where onsite, pilot-scale testing is a possibility because these costs may be substantial.

The federal agency contemplating technology solicitation should be advised that vendors may request indemnification during the demonstration. Section 119 of CERCLA (as amended) grants the U.S. President authority to indemnify response action contractors from liability when a hazardous substance, pollutant or contaminant is released from site during a response action. It is HLA's and HLA's understanding that EPA has granted vendors indemnification for such cases during SITE demonstrations.

A multiorganizational proposal review is also recommended because it was PMRMA's experience that such a review resulted in fair and objective scoring. Because of the variety of technologies that may be solicited and the multi-disciplinary nature of many of the proposed tests, a multiorganizational review process is recommended to allow review by a diversity of technical specialists.



EVALUATION OF THE USE OF PROPELLANTS AS SUPPLEMENTAL FUELS

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The United States Army Toxic and Hazardous Materials Agency (USATHAMA) is currently conducting a program with the Tennessee Valley Authority (TVA) to determine the feasibility of utilizing propellants as supplemental fuels for the U.S. Army's industrial combustors. Disposing of obsolete and waste propellants in this manner could be both cost-effective and environmentally sound, and as an added benefit, would utilize the energy value of these materials. The propellant studied during the six-month course of the initial project in this program was a nitrocellulose containing 13.15% nitrogen by weight. A series of laboratory tests were conducted to evaluate the physical and chemical characteristics, as well as the chemical compatibility, of nitrocellulose-solvent-fuel oil solutions. Unfortunately, these tests, coupled with an economic analysis, indicated that solvation and mixing with fuel oil was not technically feasible or cost effective due to the low solubility of the nitrocellulose. However, the economic analysis did indicate potential cost effectiveness using propellant-fuel oil slurries as supplemental fuels.

The objective of the second project in the supplemental fuels program was to assess the technical, economic, and safety aspects of using propellant-fuel oil slurries as supplemental fuels. The materials studied during the five-month course of this project were nitrocellulose, nitroguanidine, and a double-base propellant. A series of laboratory tests were conducted to evaluate the physical and chemical characteristics, as well as the chemical compatibility, of propellant-fuel oil slurries. Wet-grinding of the double-base propellant with fuel oil was required to prepare slurries for testing since the as-received physical form of the material was paper-thin shavings. The physical characteristics studied were density, viscosity, settling rates, and particle-size distribution. Chemical characteristics were flash and fire points, heat of combustion, and emissions, while differential scanning calorimetry was used to assess the chemical compatibility of the propellant-fuel oil slurries. The results from these laboratory tests, as well as from an economic analysis of the process, will be discussed.

The military currently has a large inventory of acceptable propellants which are obsolete due to changes in the weapon systems for which the propellants were originally produced. Additional quantities of waste propellants, i.e., propellants that do not conform to ballistic, chemical, or physical specifications, are generated during the normal process of manufacturing these materials. For example, according to the Environmental Conference proceedings of the "Hazardous Waste Minimization Interactive Workshop" sponsored by the Army Materiel Command in November 1987, 158,000 metric tons of obsolete conventional munitions are in the demilitarization inventory with a total of 249,000 metric tons projected by the year 1993.

Currently available options for disposing of obsolete or out-of-specification propellants are open-air burning, open-air detonation, or incineration (12). At the Radford Army Ammunition Plant alone, 88 metric tons of solvent-based propellants (single-, double-, or triple-base) are slowly being disposed of by Open Burning/Open Detonation (OB/OD) or incineration. However, these options are being severely constrained due to increased pressure from local, state, and national environmental groups and agencies. For example, disposing of waste energetic compounds has come to light most recently in consequence of

under interim status for incinerators under the Resource Conservation and Recovery Act (RCRA). The OBA/OD of energetic wastes requires a Subpart X permit. Subpart X operations remain under interim status until November 1992. At that time, whether or not OBA/OD operations will be allowed to continue in their current form is unknown (3).

The United States Army Toxic and Hazardous Materials Agency (USATHAMA) is currently conducting a program to develop methods and procedures for utilizing waste explosives and propellants as supplemental additives to fuels for the recovery of energy from these compounds. Preliminary testing on the explosives TNT and RDX have been encouraging. The method used to introduce these explosives as a fuel additive involved solvation and mixing with No. 2 fuel oil (4). Preliminary testing using the propellant nitrocellulose indicated that such solvation and mixing with No. 2 fuel oil (fuel oil) is not cost effective due to the fact that only relatively small amounts (approximately 2-3 weight percent) of nitrocellulose can be incorporated in the solvent-fuel oil mixture without increasing the viscosity of the resulting nitrocellulose-solvent-fuel oil solution beyond the maximum value which a conventional oil burner could reasonably handle (5,6). However, an economic analysis did indicate potential cost effectiveness of an alternative process using propellant-fuel oil slurries as supplemental fuels. There is no data to confirm the technical feasibility of using such a slurry as a feed to an industrial combustor.

Classification, Methods of Preparation, and Properties of Propellants

Three types of propellant are used in military ordinances: single-, double-, and triple-base. These propellants consist of at least one of three common base ingredients: nitrocellulose, nitroglycerin, and/or nitroguanidine. Single base propellant contains predominantly nitrocellulose; double-base propellant is a mixture of nitrocellulose and glycerin plasticizer in nitrocellulose; and triple-base propellant contains nitrocellulose, nitroglycerin, and nitroguanidine. Different grades of nitrocellulose, containing different weight percent nitrogen materials, are used in the manufacture of each type of propellant. For example, triple-base propellants are manufactured with 12.6 percent nitrogen nitrocellulose, while single-base propellant is manufactured from a blend of 12.5 and 13.4 percent nitrogen nitrocellulose. For a single-base propellant, 85-98 percent of the composition consists of nitrocellulose; for a double-base propellant, the fraction of nitrocellulose decreases to 55-78 percent, while for a triple-base propellant, only about 20-28 percent of the composition consists of nitrocellulose.

Stabilizers are frequently incorporated into nitrocellulose-based propellants to promote long-term stability and prolong the safe storage life of these materials. The chemical compounds which have traditionally been used for this purpose are basic compounds such as amines or ureas. Typical examples include ethyl centratammonium (EPA), 2-nitrodiphenylamine (2-NDPA), and 1,3-diethyl-1,3-diphenyl urea (ethyl centratammonium). Alkali salts are sometimes added to suppress "afterburning" (in rockets) and "muzzle flash" (in guns) caused by the subsequent burning in air of the combustion products CO and H₂. Examples of these alkali salts include carbon nitrate, potassium nitrate, potassium sulfate, and lead carbonate.

Structure of Nitrocellulose. Nitrocellulose is a cellulose derivative and its solid structure strongly resembles the cellulose from which it is derived (7). In the manufacture of military grade propellants, the nitrocellulose is prepared from cotton linters. Cotton linters are the material remaining on or attached to cotton seeds after the commercially valuable cotton hairs have been removed. Typical nitrocelluloses are high molecular weight (10⁵-10⁶ g/mole) polymer chains composed of anhydroglucose units, each containing up to three nitro groups. In each glucose residue of the cellulose chain there are three hydroxyl (-OH) groups, two secondary and one primary, which theoretically could result in the formation of one or more definite compounds corresponding to the successive nitration of each type of hydroxyl group in each residue. In practice, however, no such distinction of mono-, di-, or trinitrate can be made with certainty and there is no good evidence to suggest that even the primary hydroxyl group is different from the two secondary groups in regard to their relative reactivity with nitric acid. A representative formula for nitrated cellulose may be written as C₆H₇(OH)_x(ONO₂)_y, where x + y = 3. The mononitrate, x = 2 and y = 1, has a nitrogen content of 6.76 percent; the dinitrate, x = 1 and y = 2, has a nitrogen content of 11.11 percent; and the

trinitrate, $x = 0$ and $y = 3$, has a nitrogen content of 14.14 percent. In nitrocellulose with less than 14.14 percent nitrogen, the NO_2 groups are distributed randomly along the entire length of the cellulose polymer, so x and y should be regarded as average values over the entire length of the chain.

The nitrogen content determines the chemical and physical properties of any particular nitrocellulose. The great majority of nitrocelluloses which are useful for industrial purposes have nitrogen contents of approximately 12.0 percent. The more highly nitrated variety containing from 12.9-13.5 percent nitrogen, which is made for incorporation into military propellants, is known by the traditional name of "guncotton". As mentioned, nitrocelluloses used in propellants contain 12.9-13.5 percent nitrogen by weight and consequently, still have a significant number of unnitrated hydroxyl groups randomly distributed along the polymer. These unreacted hydroxyl groups strongly affect the physical and chemical properties of the nitrocellulose polymer.

Manufacture of Nitrocellulose and Single-Base Propellants. In the manufacture of nitrocellulose, the first step is the pretreatment of the cellulose (Z). Cotton linters that have been suitably purified by washing with water are dried until the moisture content is reduced from 6-7 percent to about 0.5 percent. The linters are then nitrated by the mechanical dipper process which has displaced other, more hazardous processes. The composition of the mixed acid used in this process varies depending on the type of cellulose nitrate, the degree of nitration desired, and the season of the year. A typical mixed acid composition for the preparation of guncotton from cotton linters is 60.5 percent sulfuric acid, 24.5 percent nitric acid, 4.0 percent nitrosylsulfuric acid, and 11.0 percent water.

About 1,500 pounds of mixed acid is placed in a stainless-steel nitrator at a temperature of 30°C . The nitrator is equipped with two vertical agitators revolving in opposite directions that impart motion toward the center. Approximately 32 pounds of cotton linters are added. The paddles of the agitator are designed to immediately draw the linters below the surface of the acid, away from the fume exhaust line. Nitration is exothermic, so provisions must be made to prevent the temperature from rising above 30°C . When nitration has been completed (about 20 min), the slurry is discharged through a valve in the bottom to a centrifuge, where most of the mixed acid is removed. The acid-wet, crude nitrocellulose is then forked through an opening in the bottom of the centrifuge into a drowning basin where rapid submersion in cold water takes place. The nitrocellulose must then be stabilized and purified.

Five different grades of nitrocellulose are recognized and used in the preparation of military propellants (Table I). Pyroxylin, which contains from about 8 to 12.3 percent nitrogen, consists of light yellow, matted filaments. When dissolved in 3 parts ether and 1 part alcohol, the solution is pale yellow and viscous. Pyroxylin is also soluble in acetone or glacial acetic acid and is precipitated from solution by water. Pyroxylin is very flammable and is decomposed by light. The pyroxylin used for military purposes contains 12.20 ± 0.10 percent of nitrogen. Pyroxylin is the type of nitrocellulose that was used in the manufacture of the AA2 propellant used in the second phase of this study.

Table I. Military Grades of Nitrocellulose

Type	Class	Nitrogen, Percent
Grade A	Pyrocellulose	
Type I		12.60 ± 0.10
Type II		12.60 ± 0.15
Grade B	Guncotton	13.35 minimum
Grade C	Blended	
Type I		13.15 ± 0.05
Type II		13.25 ± 0.05
Grade D	Pyroxylin	12.20 ± 0.10
Grade E		12.00 ± 0.10



In the manufacture of single-base propellants, wet nitrocellulose from the manufacturing process described above is dehydrated. Dehydration is accomplished by pressing the nitrocellulose at low pressure to squeeze out some water, adding 95 percent ethanol, and pressing further at about 3,500 pounds per square inch. A block containing 25 pounds of dry nitrocellulose and about 8 pounds of 90 percent ethanol is obtained. The wet block is broken up into small lumps by means of a rotating drum containing iron prongs and a screen. The nitrocellulose is transferred to a water-cooled dough mixer and, while in this operation, ether equal to approximately two-thirds of the weight of dry nitrocellulose is added. Any plasticizing agents and stabilizers to be included in the composition are dissolved in or mixed with the ether prior to addition to the nitrocellulose. After addition of the ether is complete, materials such as potassium nitrate are added. Mixing of the ingredients is continued for about one hour. A partially colloided mixture which resembles dry oatmeal is produced. After pressing this mixture into a block, extruding it through a macaroni press, and re-pressing it into a block again, a well-colloided material is obtained. This is placed in a graining press and extruded through a carefully designed die. The material emerges as a cord with one or more cylindrical perforations. The cord is cut into pieces of predetermined length. Removal of the volatile solvent, with shrinkage of the grains to their final dimensions, completes the manufacture of most common single-base propellants.

Nitroglycerin. Nitroglycerin, glycerol trinitrate, or 1,2,3-propanetriol trinitrate, is a clear, colorless, odorless, oily liquid with a theoretical maximum density of 1.596 grams per cubic centimeter (γ) and a molecular weight of 227.1. Nitroglycerin can be used as a solvent for other explosives; 35 grams of dinitrotoluene dissolve in 100 grams of nitroglycerin at 20°C and 30 grams of trinitrotoluene dissolve per 100 grams at 20°C. Nitroglycerin is used extensively in propellant compositions as a gelatinizing agent for nitrocellulose as well as in dynamites.

Manufacture of Nitroglycerin and Double-Base Propellants. Nitroglycerin is manufactured by nitrating glycerin with a mixed acid (γ). Several processes are currently used in the United States and Europe. These processes can be generally classified according to whether they are continuous or batch production. In batch production, high-grade glycerol is added to mixed acid that consists of 45-50 percent nitric acid and 50-55 percent sulfuric acid. The reaction between the glycerol and mixed acid is carried out in a nitrator equipped with a mechanical agitator and cooling coils that carry a brine solution of calcium chloride at -20°C. A 6,800 pound charge of mixed acid is placed in the nitrator and the glycerol is added in a small stream. Stirring is continued for a few minutes after the 50-60 minutes required to add the glycerol. The nitroglycerin is then allowed to separate completely. The lower layer of spent acid is drained off to be recycled or otherwise disposed of, and the nitroglycerin is run off into a neutralizer. An initial 40°C water wash removes most of the acid. Then a wash with a 2-3 percent sodium carbonate solution neutralizes the residual acid. Washing with water is continued until the water is free of alkali and the nitroglycerin is neutral to litmus. The yield of nitroglycerin is 230±5 parts by weight per 100 parts of glycerin.

The chemistry involved in the continuous manufacture of nitroglycerin is basically the same as that described for batch processing except the equipment is designed to allow nonstop production. The advantages of continuous processes are: faster production, better process control, lower labor costs, and, perhaps most important, safety, as a result of the smaller accumulations of nitroglycerin at any given plant location. In the United States the common practice is to nitrate mixtures of glycol and glycerol. The nitration proceeds in the same manner as with pure glycerol.

Double base propellants are manufactured by two methods. The solvent process is similar to that used for single-base propellants except that a mixture of ethanol and acetone is used as the solvent and the solvent recovery procedure is omitted because of the hazard involved in recovering solvents containing nitroglycerin. The solventless process is used when the nitroglycerin and any other colloidizing agents constitute approximately 40 percent of the composition. The AA2 propellant used in the second phase of this project was manufactured using the solventless process. In this process the wet nitrocellulose (e.g., pyroxylin for AA2) is blended with the nitroglycerin in a tank filled with water. Ethyl centralite is mixed

in and the bulk of the excess water is removed by centrifuging. The resulting paste is put in cotton bags and subjected to heated air currents to reduce the moisture content. The remaining constituents are then blended with the partly dried paste. Repeated rolling between heated steel rollers removes the rest of the water and completes colloidizing of the nitrocellulose. The thickness of the sheet formed is controlled carefully and varies with use. If the sheet is to be cut into flakes for use in small arms or mortars, the thickness is between 0.08 and 0.32 millimeter (0.003 and 0.0125 inch). Sheets to be extruded in the form of large grains for use in rockets may be as thick as 3.18 millimeters (0.125 inch). The AA2 propellant shavings used in this study are the waste material resulting from the latter extrusion process.

Nitroguanidine. Nitroguanidine is also known as picrite or guanylnitramine (Z). The compound has a nitrogen content of 53.84 percent, an oxygen balance to CO_2 of -30.8 percent, a theoretical maximum density of 1.81 grams per cubic centimeter, and a molecular weight of 104.1. The melting point of nitroguanidine varies somewhat with the rate of heating. The pure material melts with decomposition at 232°C , but values from 220° to 250°C are obtainable with various heating rates. Because of the low temperature of explosion, about $2,098^\circ\text{C}$, nitroguanidine is used in triple-base propellants that are practically flashless and less erosive than nitrocellulose-nitroglycerin propellant of comparable force. When used by the Germans in World War II in antiaircraft guns, a nitroguanidine propellant increased the barrel life from 1,700 firings to about 15,000 firings.

Manufacture of Nitroguanidine and Triple-Base Propellants. Several methods for the preparation of nitroguanidine are known (Z). The earliest method was by the direct nitration of guanidine thiocyanate with mixed acids. Guanidine thiocyanate is one of the cheapest and easiest to prepare of the guanidine salts. However, this method of production also produced sulfur compound impurities which attacked and degraded the nitrocellulose component. This lowered the stability of propellant compositions to an unacceptable degree, thus precluding early use of the compound as an ingredient in nitrocellulose based propellants. A more pure form of nitroguanidine that does not contain the sulfur compound impurities can be prepared in one of several known ways. In one method, equimolecular quantities of urea (H_2NCONH_2) and ammonium nitrate (NH_4NO_3) are fused. The product is then recrystallized from boiling water. The yield of this method is approximately 92 percent of the theoretical.

Another method of preparation involves heating a solution of equimolecular quantities of cyanamide (H_2NCN) and ammonium nitrate (NH_4NO_3) to 160°C at a pressure of 200 pounds. The product is then recrystallized from boiling water. The yield of this method is approximately 88 percent.

A third method involves the production of guanidine nitrate as a precursor to the nitroguanidine. Two reactions can be employed to produce guanidine nitrate. The first reaction is simply the reaction between guanidine ($\text{H}_2\text{NC(=NH)NH}_2$) and nitric acid (HNO_3). The second reaction is the reaction between dicyandiamide ($\text{H}_2\text{NC(=NH)NHCN}$) and ammonium nitrate (NH_4NO_3). As the guanidine or dicyandiamide can be produced from the raw materials coke, limestone, atmospheric nitrogen, and water, the production of nitroguanidine does not involve the use of special natural resources. However, a very large amount of electrical energy is required for the production of dicyandiamide or guanidine. Dehydration of guanidine nitrate to nitroguanidine is affected by adding 1 part of the nitrate to 2.3 parts by weight of sulfuric acid (95 percent) so that the temperature does not rise above 10°C . As soon as all the nitrate has been dissolved, the milky solution is poured into seven and one-half parts of ice and water. The mixture is kept ice-cold until precipitation is complete, when the nitroguanidine is caught on a filter, washed with cold water, and redissolved in 10 parts of boiling water. The nitroguanidine recrystallizes when the solution cools. The yield is approximately 90 percent of the theoretical.

The process used for manufacturing nitroguanidine triple-base propellants in the United States has been exclusively solvent extrusion. The amount of solvent used is quite low so the propellant is very soft during extrusion. The soft strands may require partial drying before cutting so that the cross section at the cut is not deformed. Removal of solvent from the triple-base propellant is rapid, possibly due to diffusion of solvent within the grain along the crystal-plastic interfaces. To make a good quality grain, low dry-

ing temperature gradients are used to avoid steep solvent gradients, which result in distortion and cracking.

Results and Discussion: Nitrocellulose-Solvent-Fuel Oil Solutions (Phase I)

The following series of tests from the first phase of this project were conducted to determine the physical characteristics of nitrocellulose-solvent-No. 2 fuel oil (fuel oil) solutions. The solubilities of smokeless-grade nitrocellulose (Hercules, Grade C, Type I, 13.15% nitrogen) in candidate solvents identified in a literature search, fuel oil, and toluene were determined. Next, the dilution ratios of nitrocellulose-solvent solutions were measured, where fuel oil was added to the mixture until precipitation occurred. Finally, the densities and viscosities of the nitrocellulose-solvent-fuel oil solutions were measured.

Solubility Tests. The so-called lyophilic colloids such as nitrocellulose pass eventually to a state of homogeneous solution in a particular solvent by means of the dual process of gelatinization and swelling. This dual process does not correspond to any process that occurs when a crystalline substance of low or moderate molecular weight forms a homogeneous solution in a solvent. As a consequence, a true solubility limit cannot be quantitatively specified for a lyophilic colloid such as nitrocellulose, and it is impossible to have a saturated solution in a single solvent. The radical differences between the physical characteristics of nitrocellulose and a typical crystalline solid arise mainly from the high molecular weight of the nitrocellulose polymer.

There is one general rule to consider when compiling a list of candidate solvents for nitrocellulose—no substance is a solvent unless its molecule contains a polar group. Acetone, which contains a polar carbonyl oxygen (C=O) group, has been shown to be the most effective solvent for nitrocelluloses of various nitrogen contents. In fact, the aliphatic ketones and the esters of the saturated fatty acids are probably the only two classes of solvents which contain at least some members that can be relied on to dissolve all nitrocelluloses of any nitrogen content (exceeding 10.5%) and of any viscosity. However, the activity of the ketones and esters has been found to decrease as the length of the hydrocarbon chain increases.

Composite solvents, made up of at least one true solvent with one or more diluents of feeble solvent power, are in practice very important because diluents are usually relatively inexpensive and the objective is always to use as much of them as possible. A composite solvent is usually a better solvent for a particular nitrocellulose than either component solvent by itself. In most cases, the limiting factor in how much diluent can be added to form a particular composite solvent is its precipitating power, i.e., how much diluent can be tolerated before the nitrocellulose precipitates from solution. Unfortunately, fuel oil possesses a great precipitating power for nitrocellulose since it is practically devoid of any polar groups within its molecular structure. As such, fuel oil can probably be used only in limited amounts as a diluent in a composite solvent for nitrocellulose.

Solubility Results from Smokeless-Grade Nitrocellulose. Based on the information presented in the above discussion, as well as additional information compiled from the literature search, five potential solvents for the smokeless-grade nitrocellulose (13.15% nitrogen content) were selected for use in the solubility tests. These five solvents were acetone, 2-butanone, tetrahydrofuran, ethyl acetate, and butyl acetate.

Each solubility test was conducted at 25°C. The maximum concentration of nitrocellulose in each solvent which could be attained in each test was limited by the ability of the solubility apparatus (8) to adequately stir the nitrocellulose-solvent solution. For example, the maximum concentration of nitrocellulose in acetone investigated in the solubility test was 7.5% by weight. Above this concentration, the nitrocellulose-acetone solution became a viscous gel and the experiment had to be terminated. In fact, for each of the other four solvents investigated in the solubility tests, a situation similar to that with the nitrocellulose-acetone solutions was encountered. The only difference was the maximum concentration of nitrocellulose attained in each solvent before a viscous gel occurred. For 2-butanone, the maximum



concentration of nitrocellulose investigated was 6.6% by weight; for tetrahydrofuran, 6.6% by weight; for ethyl acetate, 4.8% by weight; and finally, for butyl acetate, 4.4% by weight. It is important to note that these maximum concentrations of nitrocellulose attained in each solvent before the mixture became a viscous gel provided important information required before the dilution ratio tests, described in the next section, were attempted. This information was, in fact, more important for the successful completion of this phase of the project than was the definition of actual solubility limits, which as mentioned earlier is not a practical concept to invoke when discussing solutions containing nitrocellulose.

Finally, the smokeless-grade nitrocellulose was found to be insoluble in both toluene and fuel oil at temperatures of 25, 40, and 55°C. The solubility "value" in each case was <0.010 g/ml. These results are not surprising based on the fact that paraffin hydrocarbons are known to be powerful diluents for nitrocellulose solutions. The solubility of nitrocellulose in toluene was evaluated at the request of USATHAMA personnel, since toluene is currently being used as a solvent in another project to develop a process for burning fuel oil containing explosives as a supplemental fuel for use in Army industrial combustors (4).

Dilution Ratio Tests. The dilution ratio method (ASTM D 1720-88), which involves the determination of the volume of diluent liquid required to just cause precipitation of a cellulosic material from solution, is often used as a means of assessing the solvent power of solvents for high polymers, especially cellulose derivatives. The dilution ratio method also yields important technical information regarding the ability of solutions to tolerate additions of diluent liquids. The dilution ratio is defined as the total volume of diluent added to the system divided by the total volume of solvent present. In the tests described below, the diluent liquid used was, of course, No. 2 fuel oil. The five solvents investigated were acetone, tetrahydrofuran, ethyl acetate, butyl acetate, and 2-butanone.

The results from the dilution ratio tests with each solvent are summarized in Table II. The maximum concentration of nitrocellulose in each solvent was dictated by the fact that the nitrocellulose-solvent solution had to be able to be swirled by hand in order to carry out the dilution ratio test according to ASTM D1720-88 standard procedure. Guideline maximum concentrations of nitrocellulose in each solvent were previously established in the solubility tests. In fact, the maximum concentrations of nitrocellulose in each solvent investigated in these dilution ratio tests were slightly lower than those established in the solubility tests.

Solutions of nitrocellulose in butyl acetate were able to tolerate the greatest additions of fuel oil before precipitation occurred. Unfortunately, the maximum concentration of nitrocellulose which could be attained in the butyl acetate before it became impossible to swirl the solution in the flask and adequately perform the dilution ratio tests was only 4.1%, the lowest concentration of the five solvents investigated.

Higher concentrations of nitrocellulose in ethyl acetate (5.3%), tetrahydrofuran (5.4%), and 2-butanone (5.9%) could be attained before it became impossible to swirl the solutions in the flask than was the case for butyl acetate. However, the dilution ratios for various concentrations of nitrocellulose in ethyl acetate, tetrahydrofuran, and 2-butanone were each lower, respectively, than the dilution ratios found for the nitrocellulose-butyl acetate solutions.

Finally, the highest concentration of nitrocellulose in acetone (8.3%) could be attained before it became impossible to swirl the solution in the flask and effectively perform the dilution ratio experiment. Unfortunately, solutions of nitrocellulose in acetone were the least able to tolerate additions of the fuel oil diluent. More importantly, when the nitrocellulose did precipitate from solution, it formed a gelatinous mass which was difficult to redisperse in solution and which tended to coat the sides of the flask with a thick gummy film. This result highlighted a potentially serious problem which could arise if the nitrocellulose-acetone solution was mixed with a tank of fuel oil prior to being fed to a burner. Specifically, if too much fuel oil was inadvertently added to a nitrocellulose-acetone solution, thereby exceeding the dilution ratio for that particular nitrocellulose-acetone solution, then precipitation of the nitrocellulose



**Table II. Summary of Results from Dilution Ratio Experiments^a
for Solvent-Nitrocellulose (NC) Solutions**

Solvent ^b	Initial Wt. % NC	First Endpoint (ml)	Total Solvent (ml)	Second Endpoint (ml)	Dilution Ratio
Acetone	1.4	26.5	52.0	27.0	0.519
	3.7	23.5	51.0	24.0	0.471
	6.0	22.0	51.0	22.6	0.443
	8.3	20.0	52.0	21.5	0.414
Ethyl Acetate	1.2	62.0	53.0	71.0	1.340
	3.3	48.0	52.0	51.2	0.985
	5.3	42.0	53.0	44.0	0.830
	7.3 ^c	—	—	—	—
THF ^d	1.2	49.0	52.0	50.7	0.975
	3.3	46.0	53.0	47.5	0.896
	5.4	43.0	52.0	45.0	0.865
	7.3 ^c	—	—	—	—
2-Butanone	1.4	47.0	52.0	48.0	0.923
	3.7	38.0	53.0	44.0	0.830
	5.9	39.0	53.0	43.0	0.811
	7.0 ^c	—	—	—	—
Butyl Acetate	1.4	92.0	53.0	95.0	1.792
	2.8	76.0	52.0	85.0	1.635
	4.1	56.0	53.0	62.0	1.170
	5.4 ^c	—	—	—	—

^aDilution Ratios determined similar to ASTM D1720-88 with No. 2 fuel oil as the diluent.

^bInitial volume of solvent in each experiment was 50 ml.

^cMixture too viscous to swirl and effectively perform the dilution ratio experiment.

^dTHF = tetrahydrofuran.

would occur which could potentially block fuel lines or clog a burner. Such an occurrence would obviously be unacceptable.

Density Tests. The densities of various nitrocellulose-solvent-fuel oil solutions were measured at 20 and 50°C using glass hydrometers according to ASTM D 1298-85 standard procedure. The results obtained at 20 and 50°C for each type of solution are summarized in Table III. The densities of these solutions do not merit any further comment here; in fact, the main reason that the densities of each nitrocellulose-solvent-fuel oil solution was measured was to provide the data required for calculating the viscosity of each solution. The viscosity data is more informative and will be discussed in the following section.



Table III. Densities of Nitrocellulose (NC)-Solvent-Fuel Oil Solutions at 20 and 50°C

Solvent	Wt. % Solvent	Wt. % NC	Wt. % Fuel Oil	Density (g/ml) (at 20°C)	Density (g/ml) (at 50°C)
Fuel Oil	0.0	0.0	100.0	0.851	0.826
Acetone	100.0	0.0	0.0	0.780	0.739
	65.7	0.7	33.6	0.794	0.773
	66.5	1.4	32.1	0.801	0.774
	66.4	2.7	30.9	0.806	0.780
	66.3	4.1	29.6	0.814	0.785
	68.5	5.6	25.9	ND ^a	ND ^a
Ethyl Acetate	100.0	0.0	0.0	0.887	0.844
	56.5	0.6	42.9	0.860	0.834
	58.6	1.2	40.2	0.862	0.840
	56.5	1.8	41.7	0.867	0.845
	58.1	2.4	39.5	0.865	0.844
	61.4	3.1	35.5	ND ^a	ND ^a
Butyl Acetate	100.0	0.0	0.0	0.879	0.833
	39.0	0.2	60.8	0.851	0.826
	38.9	0.7	60.4	0.852	0.831
	40.3	1.0	58.7	0.850	0.829
	44.4	1.6	54.0	ND ^a	0.849
	49.1	2.3	48.6	ND ^a	ND ^a

^aND = Not determined. Mixture too thick and viscous to introduce into the viscometer.

Viscosity Tests. Very dilute solutions of nitrocellulose are low viscosity mixtures which exhibit typical Newtonian behavior in that the rate of flow is proportional to the applied stress or pressure. On the other hand, even only slightly concentrated solutions of nitrocellulose (i.e., greater than 0.5% nitrocellulose) will develop a high viscosity and exhibit pseudoplastic non-Newtonian behavior.

Nitrocellulose has been the polymeric material of choice for innumerable investigations of the viscosity of lyophilic colloid solutions. Two classic reviews of an immense volume of work were published in 1926 by McBain et al. (9,10) before the present theories regarding viscosity or rheology had developed. McBain et al. used a nitrocellulose containing 12.1% nitrogen by weight throughout all of their investigations. The viscosities of solutions of this particular nitrocellulose at concentrations of 0.3-0.5% in a long list of solvents of every possible type were measured. These researchers demonstrated that the viscosity depended on the solvent, and the conclusion of their studies was that the best solvents (i.e., those with the greatest solvent power) yielded the least viscous solutions.

This variation of the viscosity of nitrocellulose solutions with the concentration of the nitrocellulose solute is a quite general attribute of colloid solutions. Another general attribute of colloid solutions is that temperature changes result in alterations of the viscosity of the solutions, however, no simple mathematical equation between the temperature and the viscosity of the nitrocellulose solution has been proposed in the literature.



Results from Falling Ball Viscometer. To obtain atomization in an oil burner, it has been determined that the viscosity of the oil should not exceed a range of 20 to 30 centistokes at the burner tip (4). At temperatures of 20 and 50°C, the neat No. 2 fuel oil exhibited viscosities of 5.3 and 2.5 centistokes, respectively.

The viscosities of various nitrocellulose-solvent-fuel oil solutions measured at 20 and 50°C with a falling ball viscometer according to ASTM D1343-86 standard procedure are summarized in Table IV. Only the viscosity data obtained from the solutions of nitrocellulose in acetone, ethyl acetate, and butyl acetate solutions will be discussed here, because tetrahydrofuran and 2-butanone were previously eliminated from further testing based on preliminary cost analysis and safety data.

The viscosities of the nitrocellulose-acetone-fuel oil solutions increase rapidly at 20 and 50°C as the nitrocellulose concentration increases from 0.7 to 4.1 weight percent (Table IV). At a nitrocellulose concentration of approximately 1.5 weight percent in the acetone-fuel oil mixture (66.5% acetone, 32.1% fuel oil), the viscosity of this solution at 20°C will exceed the 30 centistoke upper limit to obtain atomization in a conventional oil burner. Similarly, at a slightly higher nitrocellulose concentration of approximately 1.8% by weight in the same acetone-fuel oil mixture described above, the viscosity of this solution at 50°C will exceed the 30 centistoke upper limit for use as a fuel to fire a conventional oil burner. A temperature of 50-55°C for a feed solution to an oil burner is a reasonable value.

Therefore, the conclusion of this analysis of the viscosity data for nitrocellulose-acetone-fuel oil mixtures is that a maximum concentration of approximately 2% by weight nitrocellulose in the acetone-fuel oil solution could be burned in a typical atomizing oil burner. As will be clearly demonstrated later in the economic analysis, burning even a 6% by weight solution of nitrocellulose in acetone-fuel oil would not only take an unacceptably long time to dispose of the large amount of waste and out-of-specification propellants in the military's inventory, but would also be prohibitably expensive.

Similar analyses could also be undertaken for the falling ball viscometer results obtained from the nitrocellulose-ethyl acetate-fuel oil and nitrocellulose-butyl acetate-fuel oil solutions at 20 and 50°C. However, these analyses would not be particularly informative since the economic analysis will show that ethyl acetate and butyl acetate are both significantly more expensive solvents than acetone. Therefore, only the estimated maximum concentrations of nitrocellulose in the ethyl acetate-fuel oil and butyl acetate-fuel oil solutions at 20 and 50°C will be given here.

The estimated maximum concentration refers to that value where the viscosity of the resulting solvent-fuel oil-nitrocellulose solution will exceed the 30 centistoke limit required to efficiently atomize a fuel in an unmodified oil burner. For an ethyl acetate-fuel oil solution at 20 and 50°C, the estimated maximum concentrations of nitrocellulose which could be tolerated are 0.9 and 1.5% by weight, respectively. These maximum concentrations of nitrocellulose in the ethyl acetate-fuel oil solvent system are lower than those estimated for the nitrocellulose-acetone-fuel oil mixtures (i.e., 1.5 and 1.8% nitrocellulose at 20 and 50°C, respectively) discussed above. Finally, for the butyl acetate-fuel oil solutions at 20 and 50°C, the estimated maximum concentrations of nitrocellulose which could be added before the 30 centistoke limit is exceeded are 1.1 and 1.2% by weight, respectively. Again, these maximum concentrations of nitrocellulose in the butyl acetate-fuel oil solvent system are lower than those estimated for the nitrocellulose-acetone-fuel oil mixtures discussed above. Consequently, acetone appears to have the greatest "solvent power" for the 13.15% by weight nitrogen content, smokeless-grade nitrocellulose used in this study. In fact, acetone is also significantly less expensive than either ethyl acetate or butyl acetate. Therefore, the nitrocellulose-acetone-fuel oil system will be the only one discussed later in the economic analysis.

Table IV. Viscosities of Nitrocellulose (NC)-Solvent-Fuel Oil Solutions at 20 and 50°C

Solvent	Wt. % Solvent	Wt. % NC	Wt. % Fuel Oil	Viscosity ^a (centistokes)	Viscosity ^b (centistokes)
Fuel Oil	0.0	0.0	100.0	5.3	2.5
Acetone	100.0	0.0	0.0	0.454	0.358
	65.7	0.7	33.6	4.6	2.5
	66.5	1.4	32.1	24.5	8.9
	66.4	2.7	30.9	169.5	73.3
	66.3	4.1	29.6	100.8	270.2
	68.5	5.6	25.9	ND ^c	ND ^c
Ethyl Acetate	100.0	0.0	0.0	0.547	0.409
	56.5	0.6	42.9	4.9	2.5
	58.6	1.2	40.2	50.6	14.6
	56.5	1.8	41.7	67.4	45.3
	58.1	2.4	39.5	1978.0	243.1
	61.4	3.1	35.5	ND ^c	ND ^c
Butyl Acetate	100.0	0.0	0.0	0.878	0.596
	39.0	0.2	60.8	5.3	2.5
	38.9	0.7	60.4	5.9	1.8
	40.3	1.0	58.7	10.4	1.9
	44.4	1.6	54.0	ND ^c	437.5
	49.1	2.3	48.6	ND ^c	ND ^c

^aAt 20°C.

^bAt 50°C.

^cND = Not determined. Mixture too thick and viscous to introduce into the viscometer.

Chemical Characteristics of Nitrocellulose-Solvent-Fuel Oil Solutions

The second series of tests in the first phase of this project were conducted to determine the chemical characteristics of nitrocellulose-solvent-fuel oil solutions. Heats of combustion of fuel oil and nitrocellulose-solvent-fuel oil solutions were determined as these parameters are required for the economic analysis. The heats of combustion of nitrocellulose-tetrahydrofuran-fuel oil and nitrocellulose-2-butanone-fuel oil solutions were not obtained due to considerations discussed earlier. Supplementary tests were also conducted to investigate the chemical compatibility of nitrocellulose-solvent and nitrocellulose-solvent-fuel oil solutions.

Heat of Combustion Tests. The heat of combustion is a measure of the energy released when 1 mol of a substance is oxidized at constant pressure or constant volume. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat.

Nitrocellulose, as the major ingredient of smokeless powder, occupies a key position in the field of solid propellants. The heats of combustion, as well as the heats of explosion, of nitrocelluloses prepared from cotton linters and wood pulp, and with various nitrogen contents have been reported by Taylor and



Hall (11) and by Jessup and Prosen (12). The latter authors give heats of combustion measured at 30°C with a bomb calorimeter of one sample of cellulose and four samples of nitrocellulose prepared from cotton linters, as well as one sample of cellulose and four samples of nitrocellulose prepared from wood pulp. These heat of combustion measurements are summarized in Table V.

Table V. Heats of Combustion of Cellulose, Dinitrocellulose, and Trinitrocellulose from Cotton Linters and Wood Pulp

Material	Source of Cellulose	Heat of Combustion (Btu/lb)
Cellulose	Cotton Linters	7,497
	Wood Pulp	7,511
Dinitrocellulose	Cotton Linters	4,706
	Wood Pulp	4,710
Trinitrocellulose	Cotton Linters	3,943
	Wood Pulp	3,940

Interestingly, the heat of combustion actually decreases as the degree of nitration of the cellulose polymer increases, with the heat of combustion for trinitrocellulose (14.15% nitrogen) derived from woodpulp, for example, being 3,571 Btu/lb less than the heat of combustion for cellulose derived from woodpulp.

The heat of combustion data obtained from the smokeless-grade nitrocellulose, solvents, fuel oil, and nitrocellulose-solvent-fuel oil mixtures using a bomb calorimeter according to ASTM D 240-87 standard procedure are given in Table VI.

Table VI. Heats of Combustion for Nitrocellulose, Solvents, Fuel Oil, and Selected Nitrocellulose-Solvent-Fuel Oil Solutions

Material	Heat of Combustion (Btu/lb)
Smokeless-Grade Nitrocellulose (NC) (Hercules, Grade C, Type 1)	4,100
Acetone	13,229
Ethyl Acetate	10,980
No. 2 Fuel Oil	19,500
5.8% NC-70.7% Acetone-23.5% Fuel Oil	14,175
1.4% NC-66.5% Acetone-32.1% Fuel Oil	15,115
2.4% NC-58.1% Ethyl Acetate-39.5% Fuel Oil	14,181

Supplementary Tests. Qualitative analyses of nitrocellulose-solvent and nitrocellulose-solvent-fuel oil solutions were conducted over the six month course of this project to determine if any color changes, separation of solution phases, or precipitation occurred.

Nitrocellulose-Solvent Solutions. Solutions of acetone containing 1.0-7.5% by weight nitrocellulose, ethyl acetate containing 1.0-4.8% by weight nitrocellulose, and butyl acetate containing 0.5-4.4% by weight nitrocellulose were prepared in 2 oz. glass bottles and stored on a shelf in the laboratory at ambient temperature. After five months, all of the solutions were still free of any precipitate. However, the color of the acetone-nitrocellulose solutions progressed from transparent when freshly prepared to a pale yellow shading after five months storage. On the other hand, no discoloration of the ethyl acetate-nitrocellulose or butyl acetate-nitrocellulose solutions was noted over a storage period of five months.

The light-sensitive nature of various solutions containing nitrocellulose was first noticed in the course of the early investigations of both nitrocellulose and propellant powders. For instance, Abel (12) observed in 1867 that nitrocellulose exposed to strong light eventually became acid and was converted into a brown, gum-like mass. Nitric, formic, and oxalic acids, cyanogen, and glucose could be extracted from this gum-like mass with water. Subsequent investigations have yielded little noteworthy information on the nature of the photodecomposition mechanism for nitrocellulose. However, since a batch process would likely be used to burn the supplemental fuel containing nitrocellulose, the photo-decomposition reaction which does occur in various solvents should not present any problem.

Nitrocellulose-Solvent-Fuel Oil Solutions. Fuel oil was gradually added to solutions of acetone containing 1.0-7.5% by weight nitrocellulose, ethyl acetate containing 1.0-4.8% by weight nitrocellulose, and butyl acetate containing 0.5-4.4% by weight nitrocellulose. The final concentrations of nitrocellulose in each solvent-fuel oil-nitrocellulose solution, as well as the qualitative observations made of these mixtures, are given in Table VII. These observations were made over a time period of three days.

For each solvent, at the lowest concentrations of nitrocellulose (0.2-1.2% by weight), either none or only a small amount of precipitation was observed in the solvent-fuel oil-nitrocellulose solution after three days. For the nitrocellulose-acetone-fuel oil solutions containing 1.4-5.6% by weight nitrocellulose, significant amounts of the nitrocellulose precipitated from solution as a gel-like mass on the bottom of the container over the three days observation period. This precipitate was difficult to redisperse when the mixture was agitated vigorously by hand. The same general observations were also made for the nitrocellulose-ethyl acetate-fuel oil and nitrocellulose-butyl acetate-fuel oil solutions containing elevated levels of nitrocellulose; these observations are detailed in Table VII.

At this point in the project, the accumulated technical data and preliminary results from the economic analysis strongly indicated that acetone would be the solvent of choice for a supplemental fuel composed of nitrocellulose, solvent, and fuel oil. Since the initial qualitative tests had revealed that nitrocellulose would precipitate from various nitrocellulose-acetone-fuel oil solutions upon standing for three days, another set of nitrocellulose-acetone-fuel oil solutions, identical to those listed in Table VII, was prepared. However, these samples were placed on a reciprocating shaker on low speed. In this case, these samples remained free of precipitate for at least one month, at which time the experiment was terminated. Therefore, mechanical agitation would be required if batches of nitrocellulose-acetone-fuel oil solutions were to be stored for any period of time before being fed to a burner as a supplemental fuel.

**Table VII. Supplementary Tests: Qualitative Observations of
Nitrocellulose (NC)-Solvent-Fuel Oil Solutions**

Solvent	Wt. % Solvent	Wt. % Fuel Oil	Wt. % NC	Comments
Acetone	65.6	33.7	0.7	Small amount of gel precipitate, disperses easily with agitation.
	66.5	32.1	1.4	Larger amount of gel precipitate, adheres strongly to bottom of container and does not redisperse easily with agitation. Amount of gel precipitate increases as the wt. % of NC in the mixture increases.
	66.4	30.9	2.7	
	66.2	29.6	4.2	
	68.5	25.9	5.6	
Ethyl Acetate	56.4	43.0	0.6	Small amount of gel precipitate, disperses easily with agitation.
	58.5	40.3	1.2	Large amount of gel precipitate, disperses easily with agitation but particles adhere to inside wall of the container.
	56.5	41.7	1.8	Thick, gel-like solution which easily disperses to a homogeneous solution with agitation. No gel particles adhere to container.
	58.1	39.5	2.4	
	61.4	35.5	3.1	
Butyl Acetate	38.9	60.9	0.2	Clear, fluid solution; no precipitation visible.
	39.0	60.4	0.6	Mixture begins to thicken; gel-like mass coats the inside of the container. Coating thickens and gel particles appear as the wt. % NC in the mixture increases.
	40.2	58.8	1.0	
	44.4	54.0	1.6	
	49.2	48.5	2.3	

Economic Analysis: Nitrocellulose-Containing Solutions

An economic analysis of the various solvents, No. 2 fuel oil, and solvent-nitrocellulose-fuel oil solutions was performed in this phase of the project. This analysis emphasized the cost of the solvents, fuel oil, and solvent-fuel oil solutions as well as the amount of nitrocellulose that could be dissolved in each solvent-fuel oil solution.

Initial Cost Comparison and Selection of Solvents. To begin the economic analysis, the prices of the five candidate solvents for nitrocellulose identified in a literature search were obtained from the Chemical Marketing Reporter (Vol. 235, No. 5, January 29, 1990 issue). These prices, which are based on railroad tankcar deliveries of each solvent, are as follows: acetone, \$0.30; 2-butanone, \$0.30; butyl acetate, \$0.43; ethyl acetate, \$0.41; and tetrahydrofuran, \$1.20.

At this point, tetrahydrofuran was eliminated from further consideration in this analysis for two reasons. First, the cost of the chemical was three to four times more than the other four solvents. Second, tetrahydrofuran did not exhibit any outstanding physical characteristics with the nitrocellulose, as was clearly demonstrated in the previous sections concerning the results from the physical characteristics



tests. In addition, 2-butanone was eliminated from further consideration for similar reasons. First, 2-butanone did not exhibit any outstanding physical characteristics with the nitrocellulose. Second, and perhaps more importantly, this solvent is listed as an Environmental Protection Agency (EPA) toxic substance.

Next, the costs of the three remaining solvents were compared. Acetone was obviously the least expensive solvent for nitrocellulose when compared to ethyl and butyl acetate. Furthermore, in addition to the economic advantage, acetone was able to dissolve a greater concentration of nitrocellulose (7.5%) than either butyl acetate (4.4%) or ethyl acetate (4.8%). Therefore, acetone was determined to be the most economical and technically suitable solvent for nitrocellulose.

Results and Discussion. The costs for burning a fuel oil-acetone-nitrocellulose solution compared with burning fuel oil only was determined for two solutions containing different concentrations of nitrocellulose. Equipment and labor costs were not considered in this analysis.

The weight percent compositions of the solutions chosen, 64.6% acetone-31.2% fuel oil-4.2% nitrocellulose and 64.8% acetone-29.3% fuel oil-5.9% nitrocellulose, were based on the data obtained from the dilution ratio experiments (Table II). To begin the economic analysis for each solution, the heat of combustion was calculated. Next, the quantity of each solution required to fuel each of four different boiler sizes (i.e., 20, 30, 40, and 50 MBtu/hr) was determined. Finally, the costs for burning each solution in the quantities required to fuel each boiler were calculated and compared to the costs required to fuel the boilers with fuel oil only. These comparisons are shown in Table VIII.

**Table VIII. Comparison Between Burning Fuel Oil Versus
a Fuel Oil-Acetone-Nitrocellulose (NC) Solution**

Boiler size, MBtu/hr	Mixture input, lb/hr (gpm)	Cost to burn mixture \$/hr	Cost to burn fuel oil only \$/hr	Additional cost to burn mixture over fuel oil, \$/hr	Amount of NC consumed, metric tons/yr
Part A^a					
20	1351 (3)	318	107	211	225
30	2027 (5)	477	160	317	338
40	2702 (7)	635	213	422	451
50	3378 (8)	794	267	528	564
Part B^b					
20	1377 (3)	306	107	199	323
30	2065 (5)	459	160	299	484
40	2754 (7)	612	213	399	645
50	3442 (8)	765	267	499	807

^aWeight percent of NC in the mixture = 4.2%

Dilution ratio of the mixture = 0.443

Wt. % composition of the solution = 31.2% fuel oil, 64.6% acetone, and 4.2% nitrocellulose

Heat of combustion for the mixture = 14,803 Btu/lb

^bWeight percent of NC in the mixture = 5.9%

Dilution ratio of the mixture = 0.414

Wt. % composition of the mixture = 29.3% fuel oil, 64.8% acetone, 5.9% nitrocellulose

Heat of combustion for the mixture = 14,526 Btu/lb



The data given in Table VIII clearly shows that in both cases, substantial additional costs will be incurred if the Army's boilers are fueled with a fuel oil-acetone-nitrocellulose solution instead of fuel oil alone. For example, the additional costs to burn the 64.6% acetone-31.2% fuel oil-4.2% nitrocellulose solution instead of fuel oil only are \$211/hr, \$317/hr, \$422/hr, and \$528/hr for a 20, 30, 40, and 50 MBtu/hr boiler, respectively. Similarly, for the 64.8% acetone-29.3% fuel oil-5.9% nitrocellulose solution, the additional costs to burn the solution versus fuel oil only are \$199/hr, \$299/hr, \$399/hr, and \$499/hr for a 20, 30, 40, and 50 MBtu/hr boiler, respectively.

The additional costs incurred for burning the acetone-fuel oil-nitrocellulose solutions are a combination of the following: (1) the cost of acetone is approximately \$0.20 per pound higher than fuel oil, and (2) the heat of combustion for No. 2 fuel oil is approximately 19,500 btu/lb as compared with acetone, 13,229 btu/lb, and nitrocellulose, 4,100 btu/lb. Because we are adding materials to the fuel oil with a lower btu/lb rating than fuel oil itself, the heat of combustion for, e.g., the 64.6% acetone-31.2% fuel oil-4.2% nitrocellulose solution is much lower than the heat of combustion for fuel oil only. Therefore, a larger quantity of the acetone-fuel oil-nitrocellulose solution is required to feed a particular boiler size in order to produce the energy required to fire that boiler than is the quantity of fuel oil required.

Possible Alternatives to Burning Acetone-Nitrocellulose-Fuel Oil Solutions as Supplemental Fuels. A viable alternative to burning acetone-nitrocellulose-fuel oil solutions as a supplemental fuel might be to suspend the nitrocellulose in fuel oil and burn this slurry. Consequently, a preliminary cost comparison for burning a fuel oil-nitrocellulose slurry versus fuel oil only was performed to substantiate this assumption. As in the previous section, equipment and labor costs were not included in this analysis.

For comparison purposes, arbitrary concentrations of nitrocellulose in the fuel oil were chosen between zero and thirty weight percent. The cost to burn the fuel oil-nitrocellulose slurries as a supplemental fuel were then calculated for 20, 30, 40, and 50 MBtu/hr boiler sizes. These cost comparisons are summarized in Table IX. Addition of nitrocellulose to the fuel oil decreases the cost to fuel a particular size boiler compared to the cost to fuel the boiler with fuel oil only. Specifically, considering a 20 MBtu/hr boiler, burning a mixture of 5%, 10%, 20%, or 30% nitrocellulose in fuel oil instead of fuel oil only yields a cost savings of \$31/hr, \$65/hr, \$142/hr, or \$235/hr, respectively. It is also important to note here that if, for example, a 30% nitrocellulose-70% fuel oil mixture were used to fire a 20 MBtu/hr boiler, approximately 1602 metric tons per year of nitrocellulose could be disposed of.

Furthermore, if the boiler size is increased to 50 MBtu/hr, burning mixtures of 5%, 10%, 20%, or 30% nitrocellulose in fuel oil compared to No. 2 fuel oil alone increases the cost savings to \$78/hr, \$162/hr, \$354/hr, or \$587/hr, respectively. More importantly, burning a 30% nitrocellulose-70% fuel oil slurry in a 50 MBtu/hr boiler would dispose of approximately 4,005 metric tons of nitrocellulose per year.

Recall that one of the main drawbacks of using an acetone-nitrocellulose-fuel oil solution as a supplemental fuel to fire a boiler was that only a small amount of nitrocellulose (approximately 2% by weight) could be incorporated into the solution without the viscosity rising above the maximum value which could be handled by an unmodified oil burner. Obviously, burning this type of mixture in a boiler, besides being prohibitively expensive, would only dispose of a very small amount of nitrocellulose per year. Considering the large inventory of waste and out-of-specification nitrocellulose-containing propellant in the military's disposal inventory, the alternative process described above becomes worthy of serious consideration. In fact, the technical and economic evaluation of the feasibility of using propellant-fuel oil slurries as supplemental fuels is given in the next section.

**Table IX. Comparison Between Burning Fuel Oil Versus
Fuel Oil Containing Nitrocellulose (NC)^a**

Fraction of NC (wt. %)	Fraction of fuel oil (wt. %)	Heat of combustion for the mixture, Btu/lb	Mixture input lb/hr (gpm)	Cost to burn mixture \$/hr	Additional cost to burn mixture over fuel oil, \$/hr	Amount of NC consumed, metric tons/yr
BASIS: Boiler Size = 20 MBtu/hr						
0.00	1.00	19500	1026 (2)	107	----	0
0.05	0.95	18730	1068 (2)	76	-31	212
0.10	0.90	17960	1114 (2)	42	-65	442
0.20	0.80	16420	1218 (3)	-35	-142	968
0.30	0.70	14880	1344 (3)	-128	-235	1602
BASIS: Boiler Size = 30 MBtu/hr						
0.00	1.00	19500	1538 (4)	160	----	0
0.05	0.95	18730	1602 (4)	113	-47	318
0.10	0.90	17960	1679 (4)	63	-97	664
0.20	0.80	16420	1827 (4)	-53	-213	1452
0.30	0.70	14880	2016 (4)	-192	-352	2403
BASIS: Boiler Size = 40 MBtu/hr						
0.00	1.00	19500	2051 (5)	213	----	0
0.05	0.95	18730	2136 (5)	151	-62	424
0.10	0.90	17960	2227 (5)	84	-130	885
0.20	0.80	16420	2436 (5)	-70	-283	1936
0.30	0.70	14880	2688 (5)	-256	-469	3204
BASIS: Boiler Size = 50 MBtu/hr						
0.00	1.00	19500	2564 (6)	267	----	0
0.05	0.95	18730	2670 (6)	189	-78	530
0.10	0.90	17960	2784 (6)	105	-162	1106
0.20	0.80	16420	3045 (6)	-88	-354	2420
0.30	0.70	14880	3360 (7)	-320	-587	4005

^aNegative numbers represent savings.

Results and Discussion: Propellant-Fuel Oil Slurries

The first series of tests in the second phase of this project were conducted to determine the physical characteristics of propellant-fuel oil slurries. Initially, tests were conducted to determine the feasibility of wet-grinding the AA2 propellant shavings with fuel oil to produce slurries suitable for subsequent physical testing. The as-received samples of nitrocellulose and nitroguanidine propellant did not require wet-grinding prior to dispersing them in fuel oil to form slurries suitable for testing. The solubility of each propellant in fuel oil at 25, 45, and 65°C was then measured. Next, the particle-size distributions of representative AA2 propellant-fuel oil slurries were measured. The settling rate for each propellant-fuel oil slurry was recorded. Finally, the density and viscosity of each propellant-fuel oil slurry was measured at 25, 45, and 65°C.

Characterization and Composition of Each Propellant Sample. Each propellant sample used in this project was supplied by the Naval Ordnance Station in Indian Head, Maryland. Nitroguanidine was supplied as a dry (<1 percent H₂O), finely-divided powder. Some aggregation of the nitroguanidine occurred during shipping and handling, however, these aggregates were easily broken up when the nitroguanidine was dispersed in the fuel oil. A chemical analysis for percent carbon (C), hydrogen (H), and nitrogen



(N) content confirmed the purity of the nitroguanidine sample as greater than 99 percent. The C, H, and N content was determined with a Carlo Erba Model 1108 elemental analyzer. The nitrocellulose was received as a water-wet (28-29 percent H₂O), finely-divided powder that contained 13.3 percent nitrogen by weight. Finally, the AA2 propellant was supplied as paper-thin shavings of various lengths, resulting from the extrusion of the propellant sheets through a die to form large grains for use in rockets. The composition of this propellant was kindly supplied by Hercules, Inc., Rocket Center, West Virginia (Table X). This composition was confirmed by a chemical analysis.

Table X. Composition of the AA2 Propellant Formulation

Ingredient	Weight Percent in the Formulation
Nitrocellulose (12.2 percent nitrogen)	51.0
Nitroglycerin	38.6
Triacetin	2.7
Lead Salt	4.0
Dinitrophenylamine	1.6
2-Nitrodiphenylamine	2.0
Wax	0.1

Solubility Tests. Nitrocellulose was found to be insoluble (< 0.010 g/ml) in fuel oil at 25, 45, and 65°C. As was noted in the previous report from the supplemental fuels program (5), the common paraffin hydrocarbons are very poor solvents for nitrocellulose since they are practically devoid of any polar groups within their molecular structure. As a general rule, no substance is a solvent for nitrocellulose unless its molecular structure contains a polar group. For example, acetone, which contains a polar carbonyl oxygen (C=O) group, has been shown to be one of the most effective solvents for nitrocelluloses of various nitrogen contents (14,15). Nitroguanidine was also found to be insoluble (< 0.010 g/ml) in fuel oil at 25, 45, and 65°C. Nitroguanidine is slightly soluble in water and alcohol at 25°C, but nearly insoluble in ether at this temperature. Finally, the AA2 propellant was found to be slightly soluble in fuel oil at 25, 45, and 65°C, the solubility values being 0.0145, 0.0154, and 0.0163 g/ml, respectively.

Size Reduction and Particle-Size Distribution Tests. As stated earlier, the as-received form of the AA2 propellant was as paper-thin shavings of various lengths and sizes. In order to produce a slurry suitable for subsequent physical and chemical testing, the AA2 propellant shavings were wet-ground for 5 minutes with fuel oil using an Ultra-Turrax T-25 grinder fitted with a #S25N-25F dispersing tool. The particle-size distribution from a representative AA2 propellant-fuel oil slurry prepared with this grinding apparatus is given in Table XI. This particle-size distribution was characteristic of each AA2 propellant-fuel oil slurry and did not vary significantly as the weight percent concentration of AA2 propellant in the fuel oil was increased from 5 to 30 percent.

Settling Rates of Propellant-Fuel Oil Slurries. Each propellant-fuel oil slurry was allowed to settle for approximately one week and the level to which the propellant had settled was marked on the container. Each slurry was then shaken vigorously for 30 seconds to redisperse the propellant in the fuel oil. The amount of time elapsed while the slurry settled to the marked position on the container was then recorded. For the nitroguanidine-fuel oil slurries, 60 minutes and 120 minutes, respectively, was required for 5 and 15 percent by weight propellant-fuel oil slurries to settle out. On average, for both the nitrocellulose (dried)- and nitrocellulose (as-received)-fuel oil slurries, 60 minutes was required for the nitrocellulose in the slurries to settle out, irrespective of concentration. Finally, for the AA2 propellant-fuel oil slurries, the elapsed time for the propellant to settle out averaged less than 15 minutes.



Table XI. Particle-size Distribution of AA2 Propellant After Wet-Grinding in Fuel Oil

Particle Size (micron)	Amount Retained (wt. %)	Sieve Number
420	0.4	40
250	30.5	60
177	29.3	80
125	28.2	120
90	6.0	170
45	3.2	325
-45	2.4	-325

Densities of Propellant-Fuel Oil Slurries. The density of each propellant-fuel oil slurry was measured at 25, 45, and 65°C with a mud balance according to ASTM D 4380-84 standard procedure. The results obtained at each temperature for each type of slurry are summarized in Table XII. The densities of these slurries are relatively unremarkable; in fact, the main reasons that the density of each slurry was measured was to provide the data required for calculating the viscosity of each slurry and some economic parameters as well. The viscosity data is more informative and will be discussed in the following section.

Table XII. Densities^a of Propellant-Fuel Oil Slurries at 25, 45, and 65°C

Propellant	Wt. % Propellant	Density (g/ml)		
		25°C	45°C	65°C
Fuel Oil	0.0	0.851	0.826	0.812
Nitroguanidine	5.0	0.875	0.858	0.846
	7.5	0.883	0.870	0.860
	10.0	0.901	0.885	0.871
	12.5	0.920	0.891	0.885
	15.0	0.933	0.908	0.895
Nitrocellulose (Dried at 70°C)	5.0	0.875	0.855	0.826
	7.5	0.886	0.872	0.840
	10.0	0.898	0.880	0.852
	12.5	0.908	0.886	0.870
	15.0	0.939	0.896	0.883
Nitrocellulose (28% Water)	5.0	0.872	0.859	0.847
	7.5	0.880	0.868	0.860
	10.0	0.891	0.878	0.867
	12.5	0.905	0.885	0.874
	15.0	0.910	0.893	0.883
AA2 Propellant	5.0	0.879	0.864	0.854
	10.0	0.899	0.885	0.872
	15.0	0.924	0.903	0.891
	20.0	0.943	0.926	0.911
	25.0	0.968	0.948	0.930
	30.0	0.983	0.966	0.952

^aAll values are the average of three replicates.



Viscosities of Propellant-Fuel Oil Slurries. To obtain atomization in a standard, unmodified oil burner, it has been determined that the viscosity of the oil should not exceed a range of 20 to 30 centistokes at the burner tip (4). At temperatures of 25, 45, and 65°C, the neat No. 2 fuel oil exhibited viscosities of 5.3, 4.5, and 3.4 centistokes, respectively.

The viscosity of each propellant-fuel oil slurry was measured at 25, 45, and 65°C with a Brookfield Model DV-II viscometer according to Method A, ASTM D 2196-86 and ASTM D 1439-83a standard procedures. The viscosity data is summarized in Table XIII. Two general observations can be made based upon the data given in this Table: (1) the viscosity of each propellant-fuel oil slurry increases as the weight percent concentration of propellant in the fuel oil increases; and (2) the viscosity of each propellant-fuel oil slurry decreases as the temperature is increased from 25 to 65°C.

Table XIII. Viscosities^a of Propellant-Fuel Oil Slurries
at 25, 45, and 65°C

Propellant Fuel Oil	Wt. % Propellant	Viscosity (cS)		
		25°C	45°C	65°C
	0.0	5.3	4.5	3.4
Nitroguanidine	5.0	9.3	6.5	5.7
	7.5	12.6	9.8	8.8
	10.0	31.4	18.4	16.0
	12.5	78.2	54.5	49.6
	15.0	128.9	74.4	58.6
Nitrocellulose (Dried at 70°C)	5.0	15.9	10.5	8.7
	7.5	53.5	30.4	25.0
	10.0	156.4	95.6	80.9
	12.5	381.5	203.2	180.5
	15.0	454.8	243.5	220.8
Nitrocellulose (28% Water Content)	5.0	12.4	9.8	7.8
	7.5	29.9	17.7	14.9
	10.0	54.3	40.1	33.6
	12.5	149.9	110.9	98.2
	15.0	341.9	240.5	188.0
AA-2 Propellant	5.0	43.8	20.3	17.9
	10.0	51.9	40.5	35.9
	15.0	58.0	52.1	46.4
	20.0	84.7	64.3	54.7
	25.0	92.7	78.3	69.6
	30.0	105.4	87.8	83.9

^aViscosity is the averaging of three replicates.

Before a more in-depth analysis of the viscosity data from each type of propellant-fuel oil slurry can be presented, some additional points need to be made regarding the accuracy of viscosity measurements obtained from dispersions or slurries. Dispersions or slurries, which are multiphase materials consisting of one or more solid phases dispersed in a liquid phase, display characteristics peculiar to multiphase materials. These characteristics are discussed below.

One of the major characteristics to consider is the state of aggregation of the sample material. Are the particles that make up the solid phase separate and distinct or are they clumped together; how large are the clumps and how tightly are they stuck together? If the clumps (flocs) occupy a large volume in the dispersion, the viscosity of the dispersion will tend to be higher than if the floc volume was smaller. This is due to the greater force required to dissipate the solid component of the dispersion. In fact, this provides a rationale for the first general observation noted above for the propellant-fuel oil slurries, namely, that the viscosity of each slurry increases as the weight percent concentration of propellant in the fuel oil increases.

The shape of the particles making up the dispersed phase is also of significance in determining a system's rheology. Particles suspended in a flowing medium are constantly being rotated. If the particles are essentially spherical, rotation can occur freely. If, however, the particles are needle- or plate-shaped, the ease with which rotation can occur is less predictable, as is the effect of varying shear rates. Finally, the stability of a dispersed phase is particularly critical when measuring the viscosity of a multiphase system. If the dispersed phase has a tendency to settle, producing a non-homogeneous fluid, the rheological characteristics of the system will change. In most cases, this means that the measured viscosity will decrease. This was certainly the case with each of the propellant-fuel oil slurries measured during this study. Therefore, all the viscosity measurements described below were taken immediately after the slurry sample was shaken vigorously for 10 seconds, in accordance with ASTM D 1439-83a standard procedure.

Viscosities of Nitroguanidine-Fuel Oil Slurries. The data summarized in Table XIII indicates that at a concentration of 10 percent by weight nitroguanidine in fuel oil at both 45 and 65°C, the viscosities of the slurries will be below the 30 centistoke upper limit to obtain atomization in a standard, unmodified oil burner. However, if an oil burner could be modified to allow a supplemental fuel with, for example, a viscosity double that allowed in an unmodified burner, then the viscosity data taken at 65°C indicate that a nitroguanidine-fuel oil slurry containing 15 percent by weight nitroguanidine could be burned as a supplemental fuel. In fact, the economic analysis given in a later section indicates that it may be cost-effective to consider using a modified oil burner to dispose of propellant-fuel oil slurries containing greater than 10 percent by weight nitroguanidine.

Viscosities of Nitrocellulose-Fuel Oil Slurries. Prior to preparing the first set of slurries, the nitrocellulose was dried to less than 1 percent water content by placing small portions in an oven for 24 hours at 70°C. As the data in Table XIII shows, at a concentration of 7.5 percent by weight dried nitrocellulose in fuel oil at both 45 and 65°C, the viscosities of the slurries will be at and slightly below, respectively, the 30 centistoke upper limit to obtain atomization in a standard, unmodified oil burner. By comparison, from an inspection of the viscosities of the nitrocellulose (as-received)-fuel oil slurries it is clear that the viscosity limit to obtain atomization is not exceeded until the slurry concentration increases above 10 percent by weight of the propellant. These limits for the concentration of each nitrocellulose sample in the fuel oil, i.e., 7.5 percent by weight for the dried nitrocellulose and 10 percent by weight for the as-received (28-29 percent H₂O) nitrocellulose, probably cannot be increased since the viscosities of the next highest concentration at 65°C in each case are well above even a 60 centistoke limit postulated for a modified oil burner.

Viscosities of AA2 Propellant-Fuel Oil Slurries. The viscosities of the AA2 propellant-fuel oil slurries indicate that at a concentration of 10 percent by weight AA2 propellant in fuel oil at 65°C, the 30 centistoke upper limit to obtain atomization in a standard, unmodified oil burner will just be exceeded. How-

ever, if an oil burner could be modified to allow a supplemental fuel with, for example, a viscosity double that allowed in an unmodified burner, then the viscosity data taken at 65°C indicate that a AA2 propellant-fuel oil slurry containing 20 percent by weight AA2 propellant could be burned as a supplemental fuel.

Chemical Characteristics of Propellant-Fuel Oil Slurries

The second series of tests in the second phase of this project were conducted to determine the chemical characteristics of the propellant-fuel oil slurries. Flash and fire points, heats of combustion, and emissions from the pyrolysis of fuel oil and the propellant-fuel oil slurries were measured.

Flash Points of Propellant-Fuel Oil Slurries. The flash point measures the tendency of a sample to form a flammable mixture with air under controlled laboratory conditions. It is one of the important properties which must be considered in assessing the overall flammability hazard of a material. The flash point is used in shipping and safety regulations to define "flammable" materials. Three degrees of flammability are commonly used: flammable, combustible and nonflammable. They are defined as follows:

Flammable - flash point is less than 100°F,
Combustible - flash point is greater than 100°F,
Nonflammable - flash point is not measurable.

The flash point can also indicate the possible presence of a highly volatile and flammable component in an apparently nonvolatile or nonflammable material.

The flash points of fuel oil and propellant-fuel oil slurries were measured using a Cleveland Open-Cup apparatus according to ASTM D 92-85 standard procedure (Table XIV). As stated previously, the maximum concentration of the propellants nitrocellulose and nitroguanidine that could be attained during preparation of the slurries was 15 percent by weight. However, for the AA2 propellant, the maximum concentration of this material was 30 percent by weight. The flash points of all the nitrocellulose-fuel oil and nitroguanidine-fuel oil slurries are higher than the flash point of neat fuel oil. In contrast, when the concentration of AA2 propellant in fuel oil was increased above 15 percent by weight, the flash point became lower than the flash point of neat fuel oil. Finally, the data summarized in Table XIV clearly show that each propellant-fuel oil slurry may be classified as "combustible".

Fire Points of Propellant-Fuel Oil Slurries. The fire point measures the characteristics of a sample which are required to support combustion. The fire point is defined as the lowest temperature at which a volatile combustible substance vaporizes rapidly enough to form above its surface an air-vapor mixture which burns continuously when ignited by a small flame.

The fire points of fuel oil and the propellant-fuel oil slurries were measured using a Cleveland Open-Cup apparatus according to ASTM D 92-85 standard procedure (Table XV). With the exception of the nitroguanidine-fuel oil slurry containing 5 percent by weight propellant, the fire points of all of the propellant-fuel oil slurries are less than the fire point of fuel oil. It had been a matter of some concern that measurement of the fire points of the propellant-fuel oil slurries might not be possible due to safety considerations. However, during the analysis of these slurries, the observation was made that each propellant-fuel oil slurry burned, when initially ignited and allowed to burn for 5 seconds, in an identical manner to the fuel oil.



**Table XIV. Flash Points^a of Fuel Oil and the
Propellant-Fuel Oil Slurries**

Material	Wt. % Propellant	Wt. % Fuel Oil	Flash Point (°F)
No. 2 Fuel Oil	0.0	100.0	178.0
Nitroguanidine	5.0	95.0	235.0
	10.0	90.0	219.9
	15.0	85.0	210.2
Nitrocellulose (Dried at 70°C)	5.0	95.0	210.1
	10.0	90.0	195.1
	15.0	85.0	180.0
Nitrocellulose (As-Received)	5.0	95.0	195.1
	10.0	90.0	204.8
	15.0	85.0	185.0
AA2 Propellant	5.0	95.0	204.8
	10.0	90.0	195.1
	15.0	85.0	180.0
	20.0	80.0	175.9
	25.0	75.0	170.1
	30.0	70.0	166.7

^aMeasured according to ASTM D 92-85 standard procedure.

Heat of Combustion of Propellant-Fuel Oil Slurries. The heat of combustion is a measure of the energy released when 1 mol of a substance is oxidized at constant pressure or constant volume. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either heat or power. The heat of combustion data obtained from fuel oil and the propellant-fuel oil slurries using a bomb calorimeter according to ASTM D 240-87 standard procedure are given in Table XVI. Several of the heats of combustion measured for the propellant-fuel oil slurries are used in the economic analysis which is presented later.

Emissions From the Pyrolysis of Propellant-Fuel Oil Slurries

The emissions from propellants are dependent on the pressure and temperature, and therefore also on the confinement under which the combustion reaction proceeds. For example, DeHaan (16) has pointed out that since nitrocellulose functions as a propellant by generating large quantities of gases while undergoing an explosive burning process, its true behavior is pressure dependent. In most cases, one must be content with evaluating a propellant's behavior at atmospheric pressure. The knowledge of the reaction products of combustion processes is important for several reasons:

1. To learn more about the reaction kinetics and about equilibrium or non-equilibrium burning,
2. To study the heat output,
3. To evaluate the completeness of reactions and to find out if components of the original propellant or high explosive can still be found in the residue,
4. In connection with the disposal of energetic materials, it is also of interest if the combustion leads to toxic or carcinogenic reaction products that may be emitted to the atmosphere.



**Table XV. Fire Points^a of Fuel Oil and the
Propellant-Fuel Oil Slurries**

Material	Wt. % Propellant	Wt. % Fuel Oil	Fire Point (°F)
No. 2 Fuel Oil	0.0	100.0	237.0
Nitroguanidine	5.0	95.0	250.0
	10.0	90.0	230.0
	15.0	85.0	219.9
Nitrocellulose (Dried at 70°C)	5.0	95.0	219.9
	10.0	90.0	199.9
	15.0	85.0	190.0
Nitrocellulose (As-Received)	5.0	95.0	204.8
	10.0	90.0	210.2
	15.0	85.0	204.8
AA2 Propellant	5.0	95.0	215.1
	10.0	90.0	204.8
	15.0	85.0	199.9
	20.0	80.0	196.3
	25.0	75.0	192.2
	30.0	70.0	190.0

^aMeasured according to ASTM D 92-85 standard procedure.

A qualitative determination was made of the emissions from the nitrocellulose, nitroguanidine, and AA2 propellant using a Kratos gas chromatography-mass spectrometry (GC-MS) instrument. The GC-MS spectrum of each material was obtained and then compared and contrasted to information already available in the scientific literature. The emissions expected from various propellant-fuel oil slurries were then calculated from the information already available in the literature.

Typical Emissions From the Pyrolysis of Nitrocellulose. Many studies have been reported in the literature regarding the thermal decomposition of nitrocellulose and the analysis of the emissions from this pyrolysis (17-26). To summarize, the predominant (i.e., 10%) emissions observed from the pyrolysis of nitrocellulose are NO₂, NO, CO, CO₂, and H₂O.

Minor emissions (i.e., 5-10%) are formic acid, formaldehyde, and glyoxal. Trace emissions (i.e., <5%) are HCN, N₂, N₂O, acetaldehyde, acetone, acrolein, CH₄, H₂C=CH₂, methanol, ethanol, and formamide.

In a recent study by Huwei and Ruonong (27), pyrolysis-gas chromatography was used to study the emissions from nitrocellulose. During this analysis, the nitrocellulose was pyrolyzed at a high temperature and heating rate, yielding a quick and complete decomposition reaction. Therefore, the pyrolysis of nitrocellulose during this technique was assumed to simulate its combustion. At the high temperatures used in the study by Huwei and Ruonong, it was observed that NO₂ was changed into NO. The predominant emissions detected during this analysis were CO, NO, and CO₂. Minor emissions were N₂O and formaldehyde. Trace emissions were HCN, H₂O, CH₃CHO, CH₃CH₂CHO, CH₃COCH₃, and CH₂=CHCHO.



**Table XVI. Heats of Combustion of Fuel Oil, Propellants,
and Selected Propellant-Fuel Oil Slurries**

Material	Heat of Combustion (Btu/lb)
Nitrocellulose	4,308
Nitroguanidine	4,016
AA2 Propellant	4,354
No. 2 Fuel Oil	18,947
10% Nitrocellulose 90% No. 2 Fuel Oil	17,483
15% Nitroguanidine- 85% No. 2 Fuel Oil	16,707
15% AA2 Propellant- 85% No. 2 Fuel Oil	16,758
20% AA2 Propellant- 80% No. 2 Fuel Oil	16,029

A number of studies on the mechanism of the thermal decomposition of nitrate esters (e.g., nitrocellulose, nitroglycerin, and nitroguanidine) have verified that the decomposition proceeds with homolytic cleavage of nitrate ester groups (RO-NO_2) via an autocatalytic-type reaction. This reaction is believed to proceed by a complicated series of consecutive radical reactions. Kimura (28,29) and Kubota (30) have shown that, for example, nitrocellulose initially decomposes by rupture of one of the RO-NO_2 bonds, since they are the weakest chemical bonds present, to form oxidizers (NO_2) and alkoxy radicals ($\text{RO}\cdot$). Apparently, the decomposition process occurs in the condensed phase or at least at the burning surface. The generated NO_2 oxidizes $\text{RO}\cdot$ to form peroxy radicals ($\text{ROO}\cdot$) and nitrogen oxide (NO). Finally, the last stage is the exothermic oxidation of the organic molecules by NO giving N_2 , CO_2 , CO , H_2O , etc. (29). Fifer (31) has published an excellent review of the chemistry of the decomposition of nitrate ester and nitramine propellants.

A GC-MS spectrum was obtained from the thermal decomposition of nitrocellulose taken over the temperature range from 40 to 220°C at 10°C/min. This spectrum indicated H_2O (mass 18), HCHO and NO (mass 30), and N_2O and CO_2 (mass 44) as major peaks from the pyrolysis of nitrocellulose at 220°C and the pressure within the GC-MS capillary analysis tube. For the purposes of identifying and quantifying the major emissions expected from the pyrolysis of various nitrocellulose-fuel oil slurries, we relied on the distribution of reaction products from the pyrolysis of a single-base propellant (A 5020), published by Volk (32). The emissions obtained from the pyrolysis of this propellant were as follows: H_2 (18.4%), CH_4 (0.1%), CO_2 (12.6%), N_2 (10.1%), H_2O (15.2%), and NH_3 (0.85%). HCN and NO gases were not found.

Typical Emissions from the Pyrolysis of Nitroguanidine. Nitroguanidine is one of the main components of triple-base propellant and can form large amounts of combustion gases and NH_3 when burning. Since NH_3 gas can react with NO_2 , it may consume a large amount of the NO_2 produced during the decomposition of nitrate and connected with an autocatalytic decomposition of the propellant (33). In a study by Volk (34), the following gaseous reaction products were analyzed by mass spectrometry: NH_3 , N_2O , CO_2 , N_2 , NO , NO_2 , and HCN . Temperatures in the range of 180-240°C were used during the decomposition stage of the analysis. In the gas mixture evolved, N_2O and NH_3 were the main products. The composition of the decomposition gases was found to vary widely as a function of temperature. At the beginning of the decomposition process at 180°C, NH_3 was the main product. However, at higher temperatures or with extended decomposition time, the formation of N_2O was found to increase. For example, at 220°C the formation rate of N_2O was found to exceed that of NH_3 by 3 to 1. At 240°C, the approximate composition of the emissions from the particular nitroguanidine sample used in the study by Volk was: 23% NH_3 , 66% N_2O , 5% CO_2 , and a combined total of 6% of the gases N_2 , NO , and HCN .



Table XVI. Heats of Combustion of Fuel Oil, Propellants, and Selected Propellant-Fuel Oil Slurries

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Nitrocellulose	4,308
Nitroguanidine	4,016
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**Table XVII. Estimates of the Emissions Expected From the
Pyrolysis of Selected Propellant-Fuel Oil Slurries^a**

Slurry Composition	CO ₂	H ₂ O	NH ₃	N ₂ O	N ₂ ,NO,HCN	H ₂	CO	N ₂
10% Nitroguanidine- 90% Fuel Oil	2.845	1.040	0.023	0.066	0.006	N/A	N/A	N/A
15% Nitroguanidine- 85% Fuel Oil	2.694	0.978	0.035	0.099	0.009	N/A	N/A	N/A
10% AA2 Propellant- 90% Fuel Oil	2.866	1.064	N/A	N/A	<0.001	0.010	0.029	0.014
20% AA2 Propellant 80% Fuel Oil	2.528	0.969	N/A	N/A	<0.001	0.020	0.057	0.029
7.5% Nitrocellulose- 92.5% Fuel Oil	2.932	1.075	<0.001	N/A	N/A	0.014	N/A	0.008

^aN/A = Not Applicable.

Finally, for a 7.5 percent by weight nitrocellulose (dried)-fuel oil slurry, using the emissions data published by Volk (32) for single-base gun propellant A 5020 (i.e., 18.4% H₂, 0.1% CH₄, 12.6% CO₂, 10.1% N₂, 15.2% H₂O, and 0.85% NH₃), we estimate that 2.932 pounds of CO₂, 1.075 pounds of H₂O, 0.014 pounds of H₂, 0.008 pounds of N₂, <0.010 pounds of CH₄, and <0.010 pounds of NH₃ may be emitted from the complete combustion of one pound of this supplemental fuel.

However, it must be kept in mind that these estimates for the emissions to be expected from the pyrolysis of each propellant-fuel oil slurry are based entirely upon the best information available from the scientific literature. Confirmation of these estimates will only come when the propellant-fuel oil slurries are burned in the pilot plant at HWAAP and the emissions from this pyrolysis are measured.

Chemical Compatability of Propellant-Fuel Oil Slurries

The third and final series of laboratory tests in the second phase of this project were conducted to determine the chemical compatability of each propellant dispersed in No. 2 fuel oil. The chemical compatability of the resulting slurries was evaluated using a thermal analysis technique, differential scanning calorimetry. The propagation of reaction tests on the propellant-fuel oil slurries are currently being performed. The results from these tests, as well as from a preliminary safety analysis of the process of using propellant-fuel oil slurries as supplemental fuels, will be published later.

Differential Scanning Calorimetry (DSC). The thermal decomposition of nitrocellulose has been studied for many years (38). Wolfrom et al. (39) analyzed the decomposition products from nitrocellulose by assuming that the thermally initiated rupture of the cellulose nitrate molecule yielded a series of volatile species whose relative importance was inversely proportional to the pressure of the system. Later, using spectroscopic and gravimetric techniques, Phillips et al. (40) showed that the thermal decomposition of nitrocellulose follows, in first approximation, first-order kinetics with two or three branches, suggesting that a more complex reaction process than a simple first-order one might occur. More recently, Pfeil and Eisenreich (41) studied the thermal decomposition of nitrocellulose by thermogravimetric analysis, differential thermal analysis, and Infrared and Raman spectroscopies. Their results revealed the presence of an initial autocatalytic decomposition of nitrate groups and an increase in carbonyl and hydroxyl groups up to a weight loss of 55%. Further decomposition turned out to be a second-order reaction, terminating in a charcoal-like residue. Lemieux and Prud'homme (42) used a DSC apparatus to compare the heats of decomposition of seven nitrocellulose samples, derived from wood and cotton, with various nitrogen con-

The DSC curve obtained from the decomposition of a representative AA2 propellant-fuel oil slurry showed that the exothermic decomposition peak has shifted to a peak maximum of 224.08°C, with decomposition starting at about 205°C and finishing at about 242°C. However, in contrast to the results obtained from DSC analysis of the nitrocellulose- and nitroguanidine-fuel oil slurries, the peak maximum from the decomposition of the AA2 propellant-fuel oil slurry increased by about 16°C compared to the peak maximum from the decomposition of AA2 propellant alone.

Economic Analysis

An economic analysis of burning various propellant-fuel oil slurries as supplemental fuels was performed in this phase of the project. This analysis emphasized the costs of the propellant-fuel oil slurries as well as the amounts of the propellants that could be dispersed in the slurries. The approach used to analyze the economics of propellant-supplemented fuels was to compare them to the current application in which they would be used, namely, industrial boilers. The economic analysis is broken down into three areas, raw materials, capital costs and labor costs.

Propellant-Fuel Oil Slurries. For the production of steam in an industrial boiler, the raw materials are fuel and water. For comparing supplemented to non-supplemented fuels, the water requirements and the electricity are assumed to be equal. A 20 MM Btu/hr industrial boiler operating 6570 hours per year fired with No. 2 fuel oil will be used to provide a baseline case for further comparison with supplemented fuels. The boiler is assumed to be 80 percent efficient for both the supplemented and the non-supplemented fuel. The physical properties and costs for the fuel oil and propellants used in this economic analysis are shown in Table XVIII. The baseline fuel cost is \$856,812 per year from the following calculation:

$$\begin{aligned} &2 \cdot 10^7 \text{ Btu/hr} \cdot 6570 \text{ hrs/yr} \cdot 1 \text{ lb fuel oil} / 18,947 \text{ Btu} \cdot \\ &1 \text{ gal fuel oil} / 7.31 \text{ lb fuel oil} \cdot \$0.7225/\text{gal} \\ &\text{fuel oil} \cdot 1/0.8 \text{ (efficiency factor)} = \$856,812/\text{yr} \end{aligned}$$

A fuel oil supplemented with nitrocellulose will now be compared to the baseline. Consider a fuel with a composition of 90 percent by weight fuel oil and 10 percent by weight nitrocellulose (dried). This supplemented fuel was selected for study because the viscosity of a 10 percent by weight nitrocellulose (dried)-fuel oil slurry is just below the maximum value capable of being fed to a conventional, unmodified oil burner. The cost of one pound of this supplemented fuel is \$0.089 from the following calculation:

$$\begin{aligned} &0.90 \cdot \$0.7225/\text{gal fuel oil} \cdot 1 \text{ gal} / 7.31 \text{ lb fuel oil} = \\ &\$0.089/\text{lb supplemented fuel} \end{aligned}$$

The heating value of the supplemented fuel is 17,483 Btu/lb from the following calculation:

$$\begin{aligned} &(0.90 \cdot 18,947) + (0.10 \cdot 4308) \text{ Btu/lb} = \\ &17,483 \text{ Btu/lb supplemented fuel} \end{aligned}$$

In the above estimate the heats of solution are assumed to be negligible.



**Table XVIII. Physical Properties and Costs of Fuel Oil and
Propellants Used in the Economic Calculations**

<u>No. 2 Fuel Oil</u>	
Heat of Combustion	18,947 Btu/lb
Density	7.31 lb/gal
Cost	\$0.7225/gal
<u>Nitrocellulose</u>	
Heat of Combustion	4,308 Btu/lb
Density	11.68 lb/gal
<u>Nitroguanidine</u>	
Heat of Combustion	4,016 Btu/lb
Density	13.44 lb/gal -liquid 15.63 lb/gal -dry
<u>AA2 Propellant</u>	
Heat of Combustion	4,354 Btu/lb
Density	13.69 lb/gal -liquid 16.02 lb/gal -dry

Using the two estimates given above, the yearly fuel cost for operating the same 20 MM Btu/hr boiler as in the baseline case with the 10 percent by weight nitrocellulose-fuel oil supplemented fuel can be calculated. The following calculation yields a yearly supplemented fuel cost of \$836,132 per year.

$$\begin{aligned}
 &2 \times 10^7 \text{ Btu/hr} \times 6570 \text{ hrs/yr} \times 1 \text{ lb supplemented fuel/17,483} \\
 &\text{Btu} \times \$0.089/\text{lb supplemented fuel} \times 1/0.8 \text{ (efficiency factor)} \\
 &= \$836,141/\text{yr}
 \end{aligned}$$

Therefore, the yearly fuel cost differential (negative values represent a net savings) of operating the baseline boiler with the 10 percent by weight nitrocellulose-fuel oil supplemented fuel is:

$$(836,141 - 856,812) \$/\text{yr} = -20,671 \$/\text{yr}$$

Capital Cost. The capital cost estimate assumes that the existing boiler will be used with the supplemented fuel without retrofit. This yields a zero cost for the baseline case. The major additional equipment required to burn the supplemented fuel is found in the feed system. The daily volume of supplemented fuel required for operating the 20 MM Btu/hr boiler is 3,500 gallons. Therefore, a 5,000 gallon feed system is specified for operations. The major equipment and estimated costs for the process are given in Table XIX. If the final capital cost of \$947,400 is considered over a 20 year period at 0 percent interest, the yearly capital cost expenditure is \$47,370.

Table XIX. Capital Cost Estimate for a 5000 Gallon Feed System

Item	Capacity	Cost, \$
Feed tank	5,000 gal, SS	64,200
Mix Tank	500 gal, SS	10,000
Propellant Storage Tank	2250 gal, SS	47,900
Grinder	20 hp	15,000
Agitator	15 hp	5,000
Pumps (3)	15 gpm	9,000

Total 151,100

Langs factor for solid-fluid processing plant fixed capital is 4.18 (3). A factor of 1.5 is applied to the capital cost as an estimate to account for propellant requirements not included in equipment estimates.

Capital Cost Estimate = \$151,000 * 4.18 * 1.5 = \$947,400

Labor Cost. The labor cost estimate will assume that a 2 man operation can prepare the supplemental fuel. A supervisor is included at one quarter of the work time. Table XX shows the details of the labor cost estimate, which totals \$105,000 per year.

Table XX. Labor Cost Estimate for Burning Propellant-Fuel Oil Slurries

2 operators (@ \$25,000 / yr)	\$ 50,000
1 supervisor (@ \$40,000 / yr) * 0.25	\$ 10,000
Overhead (@ 75% labor rate)	\$ 45,000
Labor Total	\$105,000/yr

Overall Cost Comparison. The additional cost to operate the supplemental fuel fired boiler is calculated as \$131,699 per year. This cost is based on the sum of the yearly fuel cost differential, capital cost, and labor cost.

$$(-20,671) + 47,370 + 105,000 \text{ \$/yr} = \$131,699/\text{yr}$$

The amount of nitrocellulose consumed per year by burning a 10 percent by weight nitrocellulose fuel oil slurry as a supplemental fuel is calculated as 751,583 pounds. This results in a total cost for nitrocellulose destruction of \$0.1752 per pound or \$350/ton.

The results of identical calculations for various weight percentages of nitrocellulose, nitroglycerine, and AA2 propellant-fuel oil supplemented fuels are shown in Table XXI.

**Table XXI. Cost of Disposal for Various Propellant-Fuel Oil
Slurries in a 20 MM Btu/hr Industrial Boiler**

	Amount of Propellant (wt %)	Heating Value (Btu/lb)	Additional Fuel Cost (\$/yr)	Propellant Consumed (Tons/yr)	Cost of Disposal (\$/ton)
No. 2 Fuel Oil	0.0	18947	N/A	N/A	N/A
Nitrocellulose	5.0	18215	142282	180	790
	7.5	17849	136639	276	495
	10.0	17483	131699	376	350
Nitroguanidine	5.0	18201	142933	181	790
	10.0	17454	133088	376	354
	12.0	17081	127145	481	264
	15.0	16707	121380	590	206
AA2 Propellant	10.0	17488	131460	376	350
	15.0	16758	118866	588	202
	20.0	16029	106100	820	129

The current cost of disposal for propellants by OB/OD is approximately \$300/ton of propellant (3). Using the data summarized in Table XXI, a comparison of the cost for destruction by OB/OD versus using 10 percent by weight nitrocellulose-, nitroguanidine-, or AA2 propellant-fuel oil slurries as supplemental fuels indicates that OB/OD is still currently the most cost effective disposal option in each case. This concentration for the nitrocellulose-fuel oil slurry is the highest that could be handled even by a modified oil burner, i.e., the viscosities of nitrocellulose-fuel oil slurries increase dramatically as the concentration of nitrocellulose in the fuel oil increases above 10 percent by weight.

However, as noted earlier, the situation could be different for the nitroguanidine- and AA2 propellant-fuel oil slurries. If an oil burner could be identified that could burn a supplemental fuel with, for example, a viscosity double that allowed in an unmodified burner, then the viscosity data summarized earlier in Table XIII indicate that 12.5 or 15 percent by weight nitroguanidine-fuel oil slurries might be burned as supplemental fuels. As Table XXI shows, the costs for burning 12.5 and 15 percent by weight nitroguanidine-fuel oil slurries as supplemental fuels are \$264/ton and \$206/ton, respectively. Obviously, these figures are less than the current approximate cost of \$300/ton for disposal of propellants via OB/OD.

Similarly, if an oil burner could be modified to allow a supplemental fuel with, for example, a viscosity double that allowed in an unmodified burner, then the viscosity data (Table XIII) indicate that AA2 propellant-fuel oil slurries containing up to 20 percent by weight propellant could conceivably be burned as supplemental fuels. Once again, as Table XXI shows, the costs for burning 15 and 20 percent by weight AA2 propellant-fuel oil slurries as supplemental fuels are \$202/ton and \$129/ton, respectively. These figures obviously represent a significant cost savings compared to disposal via OB/OD and may represent enough savings to justify retrofit of boilers with burners capable of burning viscous slurries.

Conclusions

Based on the cost comparisons discussed in the economic analysis, we conclude that fueling boilers with 10 percent by weight nitrocellulose-, nitroguanidine-, or AA2 propellant-fuel oil slurries as supplemental fuels is not cost effective at this time. The limit of 10 percent by weight concentration of propellant in the

slurry is based on the viscosity that could be handled by a conventional, unmodified oil burner. However, it should be noted that the costs of burning these slurries as supplemental fuels are only slightly higher in cost and probably considered more environmentally acceptable than disposal of propellants via OB/OD. As discussed earlier, Myler and Mahannah (3) have noted that disposing of waste energetic compounds has recently come under regulatory scrutiny in consequence of the end of interim status for incinerators under RCRA. Whether or not OB/OD operations will be allowed to continue in their current form is unknown. Therefore, burning propellant-fuel oil slurries as supplemental fuels may be a viable option for disposal of large amounts of waste and out-of-specification propellants when the status of Subpart X operations is further clarified by November 1992. Moreover, the economic analysis, in conjunction with the physical, chemical, and chemical compatibility analyses, has shown that burning propellant-fuel oil slurries as supplemental fuels could presently be a viable option for disposing of large quantities of these materials if the Army's industrial combustors could be retrofit with burners capable of handling a fuel with a viscosity, for example, double that capable of being fed to a conventional, unmodified oil burner. The existence and cost of these modified burners are one of the areas that will be investigated in the next phase of this project.

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**PILOT STUDY TO EVALUATE
HOT GAS DECONTAMINATION OF
EXPLOSIVES-CONTAMINATED EQUIPMENT**

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This publication reflects the personal view of the authors and does not suggest or reflect the policy, practices, programs, or doctrine of the U.S. Army or Government of the United States.

INTRODUCTION

The manufacture, handling, and loading of explosives at Army facilities have resulted in the contamination of process equipment, sewer systems, and buildings. Because of this residual contamination, many process items cannot be reused or disposed of as scrap. Contaminated sewer lines are also a disposal problem after they are excavated.

Previous pilot studies have shown that decontamination of structural components is possible using a heated gas to thermally decompose or volatilize explosives with subsequent incineration in an afterburner.

A pilot study to evaluate the feasibility of hot gas to decontaminate explosives-contaminated equipment was conducted at the Hawthorne Army Ammunition Plant (HWAAP) in Hawthorne, Nevada. The pilot study was conducted from 10 July 1989 to 21 September 1989.

The primary objective of the pilot study was to determine the operating conditions that effectively decontaminate explosives-contaminated equipment. Secondary objectives included determination of the following:

- The effectiveness of the treatment on various types of equipment and equipment materials (including vitrified clay pipe) previously used in the manufacture, handling, and loading of explosives.

- The effects, if any, of the treatment on the reuse of equipment used in the manufacture, handling, and loading of explosives.
- The time-temperature dependencies for the decontamination of explosives on metal and clay surfaces.

The primary explosive and propellant compounds evaluated during the pilot study included 2,4,6-trinitrotoluene (TNT); ammonium picrate (Yellow D); and smokeless powder.

A total of 10 test runs was conducted during the pilot study. Nine test runs were conducted to evaluate the feasibility of the hot gas process for items contaminated with explosives (primarily TNT), and one test run was conducted to evaluate the feasibility of the hot gas process for equipment contaminated with ammonium picrate. The operating conditions of the test runs were selected to form a temperature-residence time matrix. For tests evaluating TNT decontamination, three operating temperatures (400°F, 500°F, and 600°F) and four residence times (6 hours, 12 hours, 24 hours, and 36 hours) were evaluated. For the test run evaluating ammonium picrate, an operating temperature of 600°F and a residence time of 48 hours were used.

DESCRIPTION OF PROCESS EQUIPMENT

The process equipment used to conduct the pilot study was supplied by the government and included an air preheater, flash chamber, and afterburner. A schematic of the process equipment is shown in Figure 1.

The air preheater is a refractory-lined combustion chamber which is 20 inches in diameter and 6 feet, 5 inches in length. It is propane-fired and rated for a total heat release of 3 million Btus per hour (Btu/hr). The air preheater is equipped with a combustion air blower designed to deliver 2,000 standard cubic feet per minute (scfm) and is driven by a 1.5-horsepower (hp) motor.

The flash chamber is an existing facility at HWAAP that was modified for the hot gas pilot investigation. It is a steel structure 12.5 feet in diameter and encased in 4 to 6 feet of reinforced concrete. Two inches of fiberglass insulation are located between the steel and the concrete. The length of the flash chamber is 53 feet; however, a temporary false wall was installed to reduce the length to 30 feet. Entry into the flash chamber is controlled by a motor-driven access door constructed of 16-inch-thick concrete and steel.

Hot gas enters the flash chamber through ducting that is 18 inches in diameter and is distributed throughout the chamber by diffusers.

The afterburner is a vertical structure measuring 5 feet in diameter and 20 feet in height and is lined with 3 inches of

WESTON

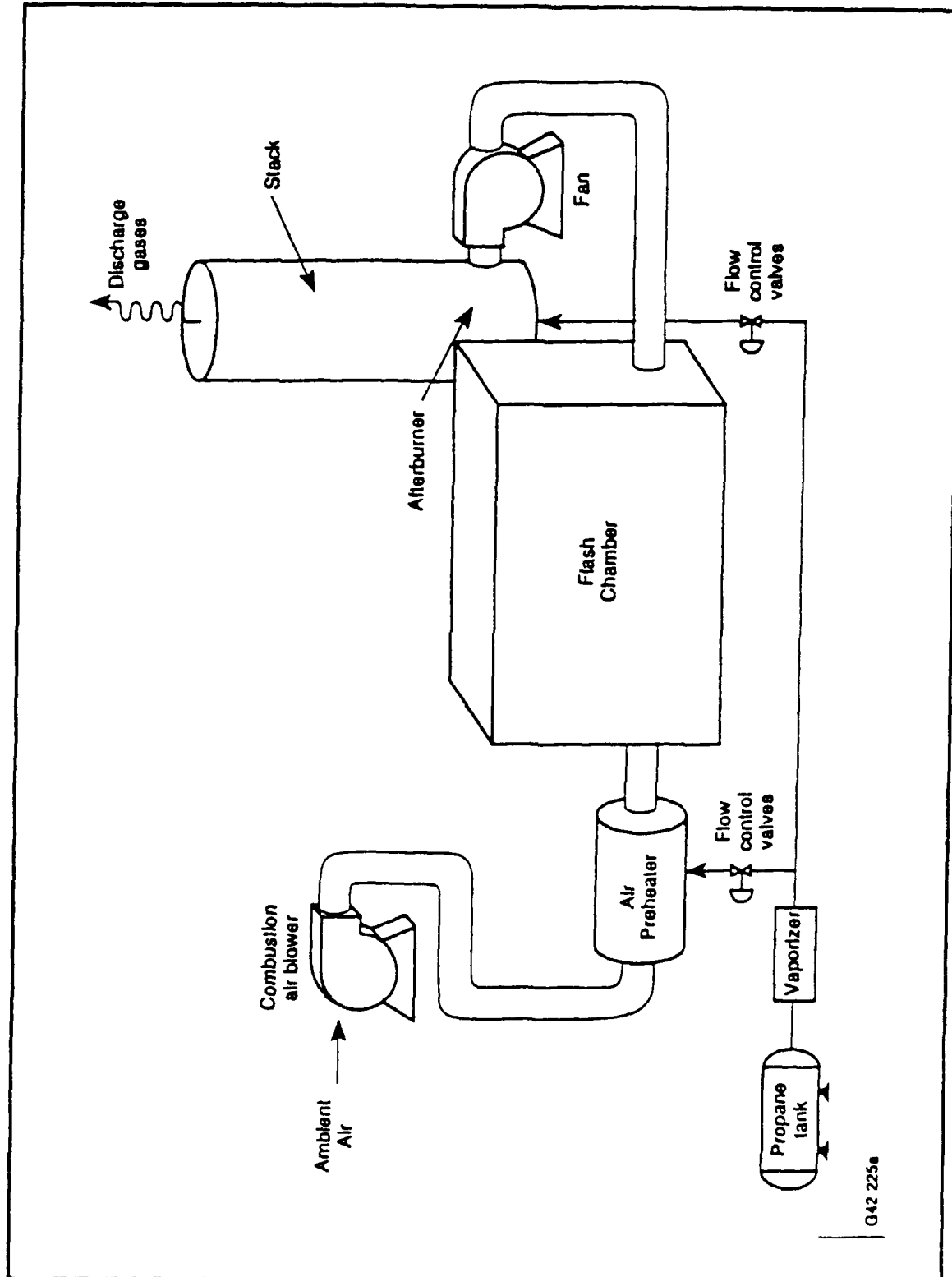


Figure 1. Schematic diagram for process equipment.

ceramic fiber insulation. The unit is propane-fired and rated for a total heat release of 4.5 million Btu/hr. The exhaust gases from the afterburner can be heated to reach a maximum temperature of approximately 2,000°F. The unit is preceded by an induced draft vent fan that withdraws gases from the flash chamber. The fan is driven by a 3-hp motor and is rated to deliver 2,200 scfm.

For each test run, explosives-or propellant-contaminated test items were placed inside the flash chamber and the chamber was securely closed. The afterburner was brought up to the appropriate temperature (approximately 1,800°F). Ambient air was blown into the preheater by means of a combustion air blower. Propane fuel was used to fire the preheater. The ambient air was heated to the appropriate target temperature in the preheater and blown into the flash chamber. The hot gas was distributed through the flash chamber by gas diffusers. The hot gas thermally decomposed or volatilized the explosives and propellant from the test items. The contaminated vapor stream was withdrawn from the flash chamber via an induced draft vent fan. The gases were directed to the afterburner, which incinerated the contaminants. Treated gases were discharged to the atmosphere. Following a cooldown period in the flash chamber, the treated test items were removed from the flash chamber and sampled.

TEST PROCEDURES

Prior to the test runs, each test item to be treated was weighed, photographed, and measured. Selected test items were sampled and then spiked with TNT or ammonium picrate.

Test items were loaded on a railcart and moved into the flash chamber. Thermocouples were attached to several test items to monitor temperatures. The chamber door was then closed and the afterburner was started. When the temperature of the afterburner reached 1,800°F, the air preheater was fired. Hot gas was directed to the flash chamber. Temperatures in the air preheater ranged from 650°F to 1,130°F, depending on the desired steady state target temperature. The target temperature was maintained in the flash chamber for the designated amount of time as determined in the test matrix. Upon completion of the steady state operation, the air preheater was shut off and the flash chamber was allowed to cool until the temperature in the chamber was safe for entry.

SAMPLING

Sampling was conducted on the test items being evaluated and on the flash chamber and afterburner gaseous emissions.

Prior to each test run, selected test items were flushed with a solvent and samples of the rinsate were collected and analyzed to determine initial concentrations. For test items too large to rinse, wipe samples were collected and analyzed. Following the decontamination, selected test items were spiked with a known

amount of explosives and placed in the flash chamber for testing. Upon completion of each test run, test items were removed from the flash chamber and sampled to determine residual explosives concentrations. For sections of vitrified clay pipe, samples were collected from sediment that had accumulated on the internal surface of the pipe. Internal concentrations of explosives in the clay pipe were determined by pulverizing a small section of pipe and analyzing the pulverized material.

To demonstrate the destruction and removal efficiency (DRE) of the afterburner, stack testing was conducted at the afterburner inlet (i.e., flash chamber outlet) and outlet. The stack sampling program was conducted to monitor the emissions of carbon monoxide (CO), total hydrocarbons (THC), nitrous oxides (NOx), particulates, explosives, and smokeless powder. Stack tests were conducted during the first three test runs.

RESULTS

TNT Testing

Based on the results of testing items contaminated with TNT, a temperature of 500°F coupled with a steady state residence time of 6 hours was determined to be the optimum condition for TNT decontamination. These operating conditions are based on the system used at the HWAAP facility, where operations included a heat-up period of 9 hours and a system cooldown period of 54 hours.

To evaluate the effectiveness of the hot gas treatment on a range of test items, various configurations and materials of construction were selected. Configurations consisted of items with external surface contamination, internal surface contamination, and contamination within porous media (vitrified clay pipe). The hot gas process was found to be effective for treating all configurations of test items. Contamination present on internal surfaces and within porous media proved to be more difficult to remove than contamination on external surfaces.

To evaluate the process on various materials of construction, test items evaluated during the pilot study were constructed of steel, aluminum, and clay. All items were visually inspected before and after each test run. Generally, items constructed of steel or aluminum showed no signs of damage due to treatment. Discoloration and scorch marks were present on some items and paint was found to crack and peel, but no flaw in the structural aspects of the items was evident. Weight loss for metallic items was negligible (if at all). However, for clay, exposure to the hot gas resulted in cracks throughout the entire pipe. The clay became very brittle and was easily broken. Prior to treatment, the soil/debris on the inside of the pipes resembled a yellow, plastic clay with some sandy material. After treatment, the material was reduced to an ash-like material. Substantial weight loss occurred to the clay pipe. Weight loss was due to the loss of water from the clay and from combustion of organic debris and explosives contained in the pipe.

Based on the results of the pilot study, test items that are contaminated with TNT and treated for 6 hours at a minimum temperature of 500°F are safe for public release as scrap. Items treated in the prescribed manner are not considered characteristically hazardous and are appropriate for disposal or potentially for resale as scrap. Treated test items that are constructed of steel or aluminum and that have no intricate or mechanical components may be appropriate for reuse in manufacture or handling operations. However, their structural stability should be verified. Treated metallic test items that have intricate or mechanical components (such as motors, pumps, etc.) are not appropriate for reuse. The mechanical integrity of these items is questionable. Internal components constructed of copper, plastic, or rubber would not withstand the sustained elevated temperatures and would be too severely damaged to function properly.

Particulate emissions measured during the first three test runs ranged from a minimum of 0.0003 lb/hr to 0.012 lb/hr. When corrected to 7% oxygen, the emissions ranged from 0.000017 grains per dry standard cubic foot (gr/dscf) to 0.00093 gr/dscf, which is two orders of magnitude less than applicable regulations.

Explosives concentrations were measured at the inlet and exit of the afterburner for the first three test runs. For all cases, the emission of TNT from the afterburner was below detectable levels. In cases where TNT inlet concentrations were sufficiently large, the DRE exceeded 99.99%.

Ammonium Picrate Testing

One test run was conducted to evaluate the decontamination of test items contaminated with ammonium picrate. It was not an objective of the pilot study to optimize conditions for ammonium picrate decontamination. Rather, the goal was to evaluate conditions expected to be effective for reducing ammonium picrate levels below detection limits. Conditions suspected of being below optimum conditions and that would leave residual contamination on the test items were not evaluated (due to potential degradation to picric acid). Operating conditions of 600 F, coupled with a steady state time of 48 hours, were found to be effective for reducing levels of ammonium picrate below detection limits.

Conclusions

The following conclusions were determined from the pilot study:

- The hot gas process is effective for treating items contaminated with TNT and ammonium picrate.
- Test items that are treated for 6 hours at a minimum temperature of 500°F are not characteristically hazardous and are appropriate for disposal or potentially for resale as scrap.

- Treated test items that are constructed of steel or aluminum and that have no intricate or mechanical components should be appropriate for reuse in manufacturing or handling operations.
- Generally, items constructed of steel or aluminum showed no signs of damage due to treatment. However, for clay, exposure to the hot gas resulted in cracks throughout the entire pipe. The clay became very brittle and was easily broken.
- Treated test items that are constructed of steel or aluminum and that contain intricate or mechanical components are not appropriate for reuse. These items should be disposed of as scrap.
- Operating conditions of 600°F, coupled with a steady state time of 48 hours, were found to be effective for reducing levels of ammonium picrate below detection limits. Optimum conditions may include lower temperatures and/or decreased residence times.
- TNT emissions from the afterburner, as measured during the stack testing program, were consistently below detectable levels. In cases where the TNT inlet concentration was sufficiently high, the DRE exceeded 99.99%.
- The emissions of particulate from the afterburner, as measured during the stack testing program, ranged from 0.000017 gr/dscf to 0.00093 gr/dscf (corrected to 7% oxygen). Emissions were two orders of magnitude lower than applicable regulations.



TECHNIQUES FOR DECOMPOSITION OF HAN

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ABSTRACT

The U. S. Army is currently investigating the use of liquid propellants in medium to large caliber guns. Olin has demonstrated the feasibility and "proof of concept" for the production of the oxidizer component, (hydroxylammonium nitrate, HAN), for liquid propellants. In the current research and development effort Olin is constructing a pilot process to demonstrate a continuous electrolytic operation producing concentrated, (13 M), HAN. The pilot process has four unit operations: **electrolysis, neutralization, concentration and waste treatment**.^{1,2}

As part of the waste treatment unit operations, techniques have been developed for decomposing the "off" specification product and control the mercury concentration of material passing to waste disposal. Several methods have been evaluated for decomposing HAN. These studies have revealed important information about stability and reactivity of HAN. HAN is a stable material under most conditions. The decomposition process is tailored to take advantage of the optimum conditions for oxidation of HAN.

Mercury waste removal after HAN decomposition requires specific steps for its removal from the solution stream, thus a selective process has been developed for mercury removal. This paper discusses only the HAN Decomposition Process.

Characterization of both process steps are integrated into the design of the Demonstration Facility.

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INTRODUCTION

Hydroxylamine salts and their solutions are of great industrial importance as intermediates, such as in the production of caprolactam, purification of plutonium metal and in photography as a reducing agent, and finally as the oxidizer for a new hydroxylammonium nitrate, HAN, based liquid gun propellant.

FORMATION

High purity hydroxylammonium nitrate, HAN, for propellant is produced electrochemically from one of the most powerful monobasic acids, nitric acid. Nitric acid, HNO_3 , is therefore very active chemically and usually behaves as an oxidizing agent at high concentrations, i.e. over one molar, and thus is itself reduced. During the reduction process, either chemical or electrochemical, there may be produced nitrous acid, nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, ammonia, hyponitrous acid, hydroxylamine and nitrohydroxylaminic acid, $\text{H}_2\text{N}_2\text{O}_3$, however; special conditions are required to produce and to isolate any one of these products. J. Tafel observed that while nitric acid is reduced only to hydroxylamine by mercury or a well-amalgamated electrode, a copper cathode reduces it completely to ammonia³. Hydroxylamine, together with dihydroxylammonia can be regarded as intermediates in the oxidation of ammonia. Figure 1 shows the oxidation sequence from ammonia, to hydroxylamine, to dihydroxylammonia and finally to the unstable orthonitrous acid, which could exist only as an unstable intermediate⁴.

The reduction path for nitric acid was shown by Angeli⁵, and V. Schvonen⁶ later made the connection between nitric acid reduction and hydroxylamine formation. This information along with the interrelationships between reduction, oxidation, hydration and dehydration for nitric acid in contact with reactive metals or electroactive electrodes is symbolized in Figure 2 according to Joss⁷. In this figure the lines which are directed vertically downward represent reduction; and horizontal lines the gain or loss of water. The reduction due to hydrogen is assumed to involve chemical or electrochemical hydrogenation by addition of one or moles of hydrogen to the compounds reduced. This chart shows that starting from nitric acid with a +5 oxidation state on nitrogen, the addition of 6 electrons will produce hydroxylamine, with a -1 oxidation state on the central nitrogen moiety after moving through the transitional species $\text{H}_x\text{N}_2\text{O}_y$, where x ranges from 2 to 10 and y from 5 to 2. Figure 3 outlines the overall electrochemical process for producing the HAN, where the cathodic portion is involved with reduction of the nitrate, followed by an acid-base neutralization with an extra mole of nitric acid to form the HAN. At a pH of 2 or less, nearly all the HAN is in the $(\text{NH}_3\text{OH})^+$ form. As the pH is raised progressively, more HAN is converted into free base (NH_2OH) , and at a pH of 6 nearly half is in this form.

DECOMPOSITION

HAN Decomposition Using Chlorine in Excess Acid

Halogen compounds of nitrogen in the form of binary halides such as nitrogen trichloride, NCl_3 , are readily formed when **chlorine is added to acid solutions of ammonia** or ammonium compounds, as shown in Figure 4. The chloride, NCl_3 , is **formed during the chlorination of slightly acidic solutions of NH_4Cl** which may be extracted into CCl_4 . When pure, it is pale yellow in the form of an oil with boiling point of

71°C. It is endothermic, with 232 kJ/mol heat of formation⁸, explosive, photosensitive and shock sensitive. Thus, its **formation should be avoided** at all costs.

HAN Decomposition Using Hypochlorite in Excess Alkali

Acidic aqueous solutions of hydroxylamine are stable, and decompose slowly above 80°C. The solutions of hydroxylamine and its salts are radical traps, whereby nitrogen and ammonia are formed. Decomposition can be promoted by heavy metal impurities such as copper, and the acidified salts react with alkali to give easily decomposed hydroxylamine.

Oxidation of hydroxylammonium salts leads to nitrogen compounds in various oxidation states, depending on the oxidant and reaction conditions, as was seen in Figure 2. The products of the alkaline hypochlorite reactions with HAN are readily disposed of through permitted discharges. Technology for proper disposal of nitrate has been demonstrated.⁹ The process for decomposing a solution of HAN comprises raising the pH to about 8 or greater and reacting the solution with a non-gaseous source of hypochlorite ion. Figure 2 indicates that the transitional species necessary to produce nitrous oxide is the hyponitrite, $\text{H}_2\text{N}_2\text{O}_2$; and for the nitrogen alone, the very unstable reduction product of hyponitrite, $\text{H}_4\text{N}_2\text{O}_2$. Since this latter intermediate is so unstable, the oxidation of HAN moves to both points giving nitrogen species in both 0 and +1 oxidation states, and thus produces both N_2 and N_2O in the process, shown in Figure 5.

EXPERIMENTAL

The hydroxylammonium salts which can be treated by this patent pending Olin process include hydroxylammonium sulfate, chloride nitrate, phosphate and perchlorate. Since the solutions of each of these salts are acidic, it is necessary to raise the pH of the solutions to where the treatment with the source of hypochlorite ion will be effective and that no residual chlorine is present to form the trihalomethanes, i.e. NCl_3 , as shown in Figure 4.

The nitrogen trichloride forms an explosive yellow oil which is sensitive to temperature and shock. It must be avoided at all costs by keeping the system alkaline in the presence of Cl_2 and NH -compounds. The product in a solution containing chlorine and ammonia or ammonium groups at $\text{pH} < 3$ is nitrogen trichloride, NCl_3 , a very volatile, unstable, explosive, oil with a pungent odor resembling chlorine; at pH 3 to 5 dichloramine forms, NHCl_2 ; finally at $\text{pH} > 8$ monochloramine, NH_2Cl . Thus, **acid conditions during mixing of chlorine and HAN must be avoided at all costs!** Figure 5 shows the observed reaction chemistry under alkaline conditions.

In a typical experimental run, 200 ml of a solution containing 0.48 moles of HAN is added to the reaction vessel equipped with an effective, inert stirrer and 30 mls of 50% caustic soda is added. With the pH at 12.2 after adding the alkali, 200 ml of 10% hypochlorite is added to the reactor from a graduated cylinder this is followed by a copious gas release, and total decomposition of the HAN.

Figure 6 is a graph of the data from three runs reacting sodium hypochlorite with HAN in different molar ratios and increments. With very fast addition rates the decomposition becomes less efficient, but with the smaller addition rates of hypochlorite to HAN, the utilization of hypochlorite becomes more efficient and the stoichiometry begins to match closer to that given for the reactions shown in Figure 5.

The Data Table in Figure 7 shows the percentages of the HAN decomposition in the gas phase after addition of a quantitative amount of hypochlorite to a batch of HAN. The appearance of a very slight amount of nitric oxide in the off-gas indicates that very fast hypochlorite addition rates can even push the oxidation potentials high enough to give traces of +2 nitrogen, in the form of nitric oxide, NO, which is another reason for their avoidance.

SUMMARY

An effective, economic process with patent pending has been developed by Olin for decomposing off-specification or waste HAN using alkaline hypochlorites.

The chlorine-nitrogen reaction chemistry for the HAN decomposition process involves a complex, interrelated sequence of redox steps. To ensure that undesired and dangerous by-products do not form, the pH must be maintained well into the alkaline region throughout the entire process to avoid the combination of Cl_2 and NH-compounds, and the subsequent formation of NCl_3 .

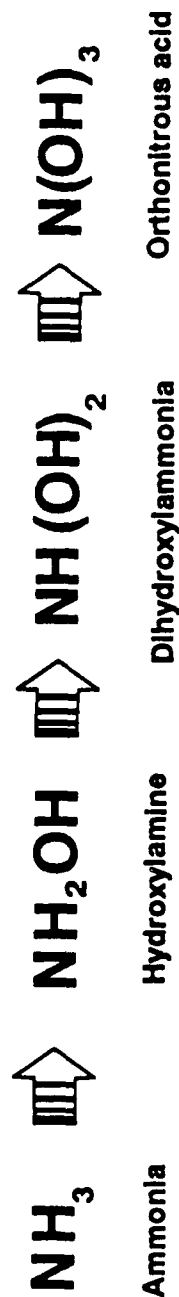
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9. Murphy, A.P. *Chemical removal of nitrate from water*, U. S. Department of the Interior, Bureau of Reclamation, Denver, Colorado, *Nature* Vol. 350, March 21, 1991.



BACKGROUND

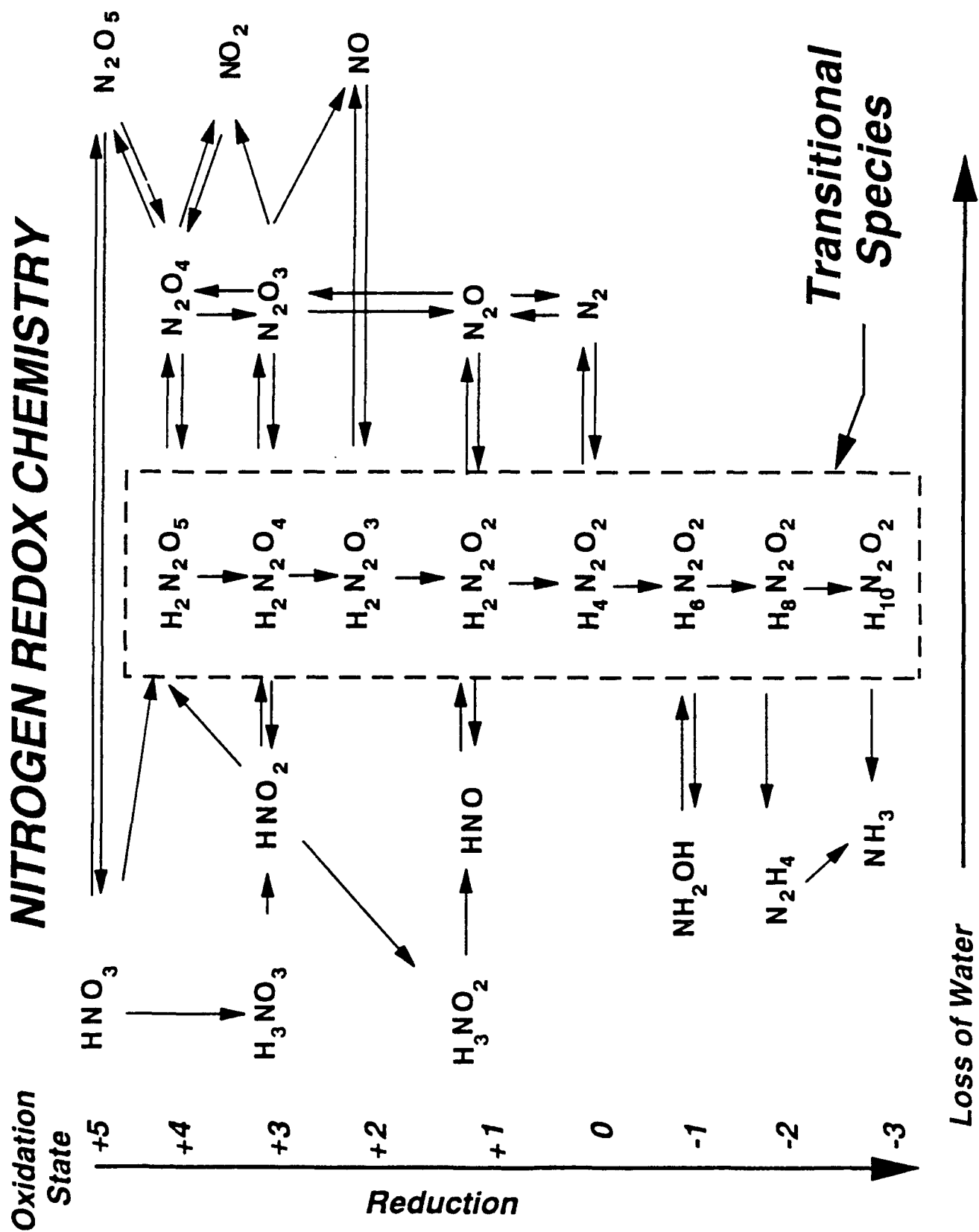
Hydroxylamine, together with dihydroxyammonia can be regarded as intermediates in the oxidation of ammonia:



Olin

FIGURE 1

FIGURE 2



HAN ELECTROLYTIC FORMATION

FROM NITRIC ACID

REACTIONS:

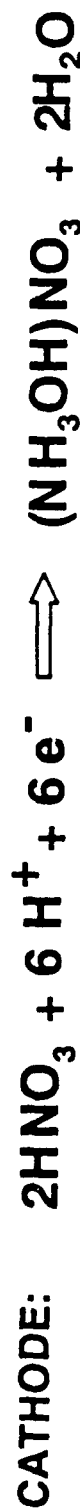
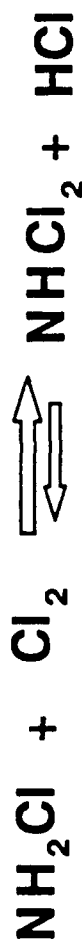
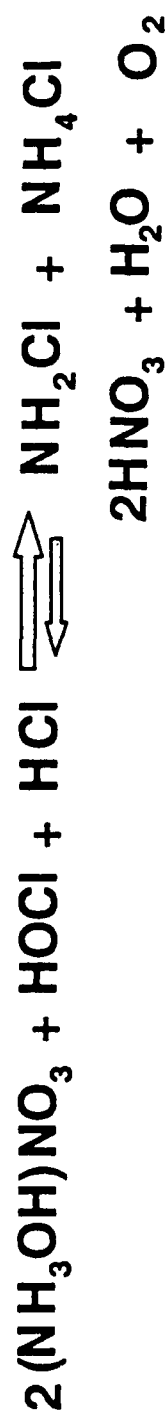


FIGURE 3

HAN DECOMPOSITION REACTION

USING CHLORINE AND XS ACID

REACTIONS:



*Explodes at 95 C
or with shock*

HAN DECOMPOSITION REACTION

USING HYPOCHLORITE AND XS ALKALI

REACTIONS:

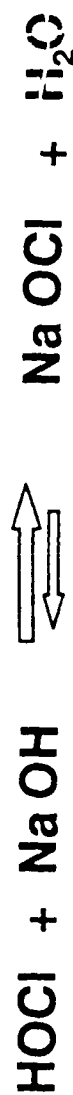


FIGURE 5

HYDROXYLAMMONIUM NITRATE DECOMPOSITION WITH SODIUM HYPOCHLORITE

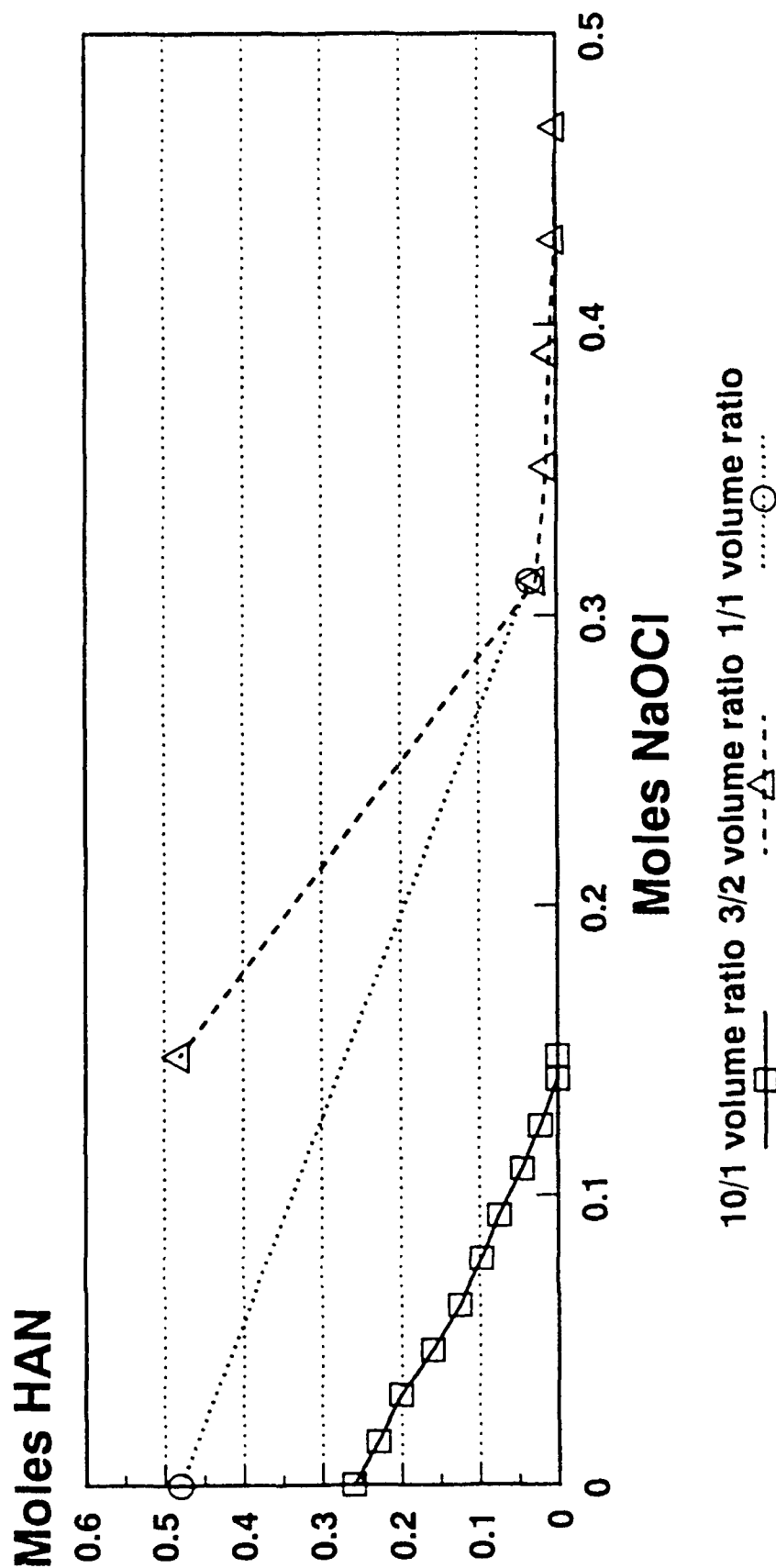


FIGURE 6

10% NaOCl
50% NaOH for pH adjustment

HAN DECOMPOSITION PRODUCT GASES

USING HYPOCHLORITE AND XS ALKALI

GAS	VOLUME PERCENT
H₂	0
O₂	0.41
N₂	52.2
N₂O	41.4
NO	0.31

FIGURE 7

15th Annual Army Environmental R&D Symposium

**TECHNOLOGY TRANSFER FROM
GOVERNMENT R&D FACILITIES**

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June 27, 1991

MARTIN MARIETTA

Restoring America's Competitive Edge

- The United States faces a serious challenge to its future competitiveness from our European trading partners and emerging nations of industrial significance in Asia and Latin America.
- We must restore our industrial productivity and competitiveness.
- Technological innovation and continued R&D is vital to our future.
- U. S. DOE is opening their labs to industry and encouraging technology transfer programs.

MARTIN MARIETTA

Environmentally Compliant

- The U. S. manufacturing industry faces increasingly rigorous compliance requirements which increase costs and impair their competitiveness in the global market.
- EPA, State, and Local government regulations.
- DOE's Office of Technology Development is providing environmental technologies and R&D programs to industry.

MARTIN MARIETTA

Technology Transfer Laws Since 1980

- Stevenson-Wydler Technology Transfer Act of 1980
- Bayh-Dole Act of 1980
- Federal Technology Transfer Act of 1986
- Technology Competitiveness Act of 1988
- National Competitiveness Technology Transfer Act of 1989

MARTIN MARIETTA

Martin Marietta Energy Systems, Inc.

Manages Oak Ridge, Tennessee Facilities for The Department of Energy

- Oak Ridge National Laboratory - 5,461 Employees, 1,200 PhDs
- Oak Ridge Y-12 Plant - 7,684 Employees
- Oak Ridge K-25 Site - 3,326 Employees (Formerly the Oak Ridge Gaseous Diffusion Plant)
- Paducah, Kentucky Plant - 1,840 Employees
- Portsmouth, Ohio Plant - 2,561 Employees

MARTIN MARIETTA

Technology Transfer

- Technology Licensing
- Partnership Development
- Economic Development

MARTIN MARIETTA

Licensing Program

Technologies Ready for Commercialization

- Identify technologies with commercial potential
- Conduct market opportunity analyses
- Fund technology maturation projects if needed
- Develop and implement licensing strategies
- Request waiver from DOE
- Negotiate licenses with industry

MARTIN MARIETTA

Technology Transfer

Technology Licensing

- Inventors become entrepreneurs
- Licensing creates a local industry
- Technology increases U. S. competitiveness

MARTIN MARIETTA

Royalty Sharing

- Royalty Fund used to Further Technology Transfer
 - Recover patenting and licensing costs
 - Reward inventors and technical staff
 - Fund technology maturation projects
 - Contribute to nonprofit technology transfer organizations
 - Pay federal income taxes
- Martin Marietta Corporation derives no monetary benefit

MARTIN MARIETTA

Technology Transfer

Types of Licenses Authorized

- Non-Exclusive
- Partially Exclusive
 - Only when necessary to induce investment of risk capital
- Exclusive
 - Only when necessary to induce investment of risk capital

MARTIN MARIETTA

Office of Technology Transfer

Licensing Program Highlights from 1985-1991

- Leading M&O Contractor in Licensing Technology to the Private Sector
- Fifty-two Active Licensing Agreements
- More than \$1.4 Million in Royalty Income
- More than \$37 Million in Licensed Product Sales
- More than \$216,000 in Royalty Income awarded to Employees

MARTIN MARIETTA

Technology Transfer

Economic Development

- More than \$94 million in private-sector capital investment since 1985
- More than 60 corporations new to Oak Ridge since 1985
- Local hotels, restaurants, retail businesses, and real estate experiencing consistent, strong growth
- Housing construction at a record high in each of the past three years
- Oak Ridge is an excellent example of what successful technology transfer can do for local economies in particular

MARTIN MARIETTA

Technology Transfer

Partnership Development Program

- Interaction Mechanisms with Industry
 - Guest Researchers
 - Employees Consulting with Industry
 - R&D in User Facilities
 - Work for Others (funds in)
 - Subcontracts (funds in)
 - Collaborative R&D (no funds exchanged)

MARTIN MARIETTA

What is a CRADA?

CRADA - Cooperative Research and Development Agreement

- Joint R&D Agreement - Between one or more Federal labs, and one or more non-Federal parties
- Shared Resources - Funds (no funds out), personnel services, facilities, equipment, other resources
- Partners - Industry, universities, non-profits, state and local governments, U. S. preference, small business consideration.
- Intellectual Property - Class advanced waiver, negotiate partner's rights, data protection up to 5 years

MARTIN MARIETTA

CRADA SIGNIFICANCE TO ENERGY SYSTEMS

- First DOE authorized M&O contractor to use CRADAs with private industry
- CRADAs provide mechanism to:
 - Leverage scarce R&D resources
 - Share complementary capabilities
 - Transfer technology during R&D phase
 - Bridge R&D/commercialization gap

MARTIN MARIETTA

Environmentally Compliant Manufacturing

Oak Ridge Y-12 Developed Programs

- Remediation of Industrial Wastes
- Environmentally Benign Solvents in Manufacturing
- Metal-Working Fluids
- Waste Minimization Through Recycle and Reuse
- Plating Operation Emissions

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Technology Transfer

Environmental Technologies and Applications

- Geophysical Diffraction Tomography
- Radiological Performance Assessment for Low-Level Waste Disposal Facilities
- Models to Handle Soil Contaminated by Radionuclides and Hazardous Chemicals
- Bioreactor to Degrade TCE and DCE
- Landscape Pattern Analysis
- Advanced Monitoring/Chemical and Biological Screening Techniques
- Advanced Monitoring/Biological and Chemical Sensors

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Technology Transfer

Environmental Technologies and Applications (cont.)

- Environmental Measurements
- Real Time Remote-Controlled Environmental Survey Systems
- Personal RF Dosimeter
- Ruggedized Alpha Detector
- Groundwater Cerenkov Radiation Detector
- Microwave Processing of Radioactive Waste
- Bioremediation
- Polymer-Impregnated Grout

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Technology Transfer

Environmental Technologies and Applications (cont.)

- In Situ Soil Venting
- Grout Meter
- Sludge Handling
- Characterization Sites Field Analytical Methods
- Real Time Monitor for Organics
- In Situ Fiberoptic Derivative Ultraviolet Absorption Spectroscopic Monitoring of Aromatic Contaminates
- Bioremediation of the Organic Contaminant of Groundwater

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Technology Transfer

Environmental Technologies and Applications (cont.)

- Low-Level Radioactive Waste Management
- Destruction of PCBs in Mixed Waste
- Removal of Hazardous Organics from Wastewater Sludges
- Dry Fluidized Bed Flue Gas Treatment Technology
- Denitration of Low-Level Waste
- Substitution of Chlorinated Hydrocarbons

MARTIN MARIETTA

VALIDATION AND USE OF U.S. ARMY HAZARDOUS WASTE (HW) GENERATION DATA FOR HW MINIMIZATION PROGRAMS

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Introduction

The Resource Conservation and Recovery Act (RCRA), amended as Hazardous and Solid Waste Amendments (HSWA) of 1984 requires hazardous waste (HW) generators to implement a waste minimization program. The Department of the Army (DA) HW minimization goal is to achieve a 50 percent reduction in HW generation by the end of calendar year 1992 (CY 92) as compared to the "baseline" year of 1985.⁽¹⁾ The Army Environmental Office compiled a HW (HW) generation baseline data and published a program status report.⁽²⁾

This program status report was based on the responses by Army installations to a message from the Army environmental Office (AEO) dated November 1987 that requested each installation to supply information on: HW generation quantities; types; quantities treated, disposed of, or recycled; minimization actions planned or implemented; and associated costs. The program status report's summary of results showed that the Army HW generation quantity in 1985 (the baseline quantity for the Army HW minimization program) was 59,630 tons and that the quantities in 1986 and 1987 were 64,613 tons (an 8 percent increase from the baseline), and 88,264 tons (a 48 percent increase from the baseline), respectively. Considering the Army's emphasis on and achievement in the HW minimization, the increase in generation quantities deserve attention. In FY90, the U.S. Army Construction Engineering Research Laboratory (USACERL) validated this data in published report.⁽³⁾ This paper summarizes the results of that report.

The objectives of investigation were to support the Army HW minimization program by critically examining the DA's HW minimization baseline data to identify problems and to recommend improvements in the way the Army collects, compiles, and distributes HW data.

Data Validation

Eight installations were selected for interview including Headquarters Army Materiel Command (AMC), three AMC installations, one Forces Command (FORSCOM) installation, Headquarters, Training and Doctrine Command (TRADOC), two TRADOC installations, and one Defense Reutilization and Marketing Office (DRMO). A questionnaire was developed and sent to each site. The results of the questionnaires were used as a basis for the interviews. The interviews focused on the rationale for the each installation's response to the AEO message.

The interview results are summarized with five major questions:

1. Do similar installations report similar generation? Where they do not, why not? Do some sites underreport some wastes? Do all respondents report on the same basis?



Some installations regarded the AEO message as a simple reporting requirement and did not carefully prepare the data. However, some installations routinely kept detailed generation information and reported HW generation quantities accurately.

The AEO message asked that the data be categorized in accordance with 40 CFR, Part 261, the U.S. Environmental Protection Agency (USEPA) list of HW. Not all installations have the knowledge and system needed to analyze and adequately characterize HW. For those that do not, this complicates the identification procedure.

Because of the way the questions on generation of wastes were asked in the AEO message, there was some confusion and misinterpretation of the message at the installations. HW generation quantities were reported with different definitions. Some installations reported only disposal quantities while others reported all recycled quantities. Also, there was some confusion between the "generation quantity" and quantity "turned in for disposal."

2. Are the absolute as opposed to the relative quantities reported credible? If not, why not?

The AEO-requested hazmin reporting by installations was analyzed and subjectively classified by three categories: good, partial, and inadequate. The criteria were: completeness, correct data format, accuracy of calculations or summaries, and data relative to known operations and installation size. Of 112 replies, less than 50 percent of the responses were "good"; the apparent overall accuracy of the data is unreliable. Closer examination of the data by year shows 1985 to be the poorest, 1986 slightly better, and 1987 the most accurate and complete. The AMC's HW data, which accounts more than 90 percent of the total Army generation, is considered to be in the good category, especially in 1987.

Armywide data from 1985 was not always available because: (1) records were not maintained and kept from 1985, (2) responsibility for HW management was switched between directorates so that records for 1985 data were lost or destroyed, (3) personnel were unfamiliar and inexperienced with HW identification and reporting, and (4) small quantity generators have not been required to report their generation levels so records concerning turn-in and disposal of hazardous materials/wastes were not maintained.

Some installations considered all material as HW when turned into the DRMO even if it was recycled, transferred, disposed of, or sold (RTDS). Some installations turned the HW in to the DRMO, then considered the DRMO responsible for the waste and credited themselves for a minimization action. On the other hand, some installations followed the HW to its final fate and reported the data accurately, as requested in the AEO questionnaire. Some installation environmental offices are still unsure about how and what to report when items are turned in to the DRMO. Some still report material turned in as the generated amount, some use the manifest totals as disposal numbers even if they contain other agencies' waste, and others take credit for minimization even if the waste is ultimately disposed of by the DRMO.

3. Is all waste reported under a given category comparable? Is there an appropriate balance between aggregation and disaggregation of wastes such that the information needed to make good decisions is available?

Accurate classification of Army HW is not easy because the waste is often a mixture of more than one HW. Most Army installations use USEPA Waste Identification Numbers to identify and report HW being generated, after chemical analysis. Since some states are more restrictive than the USEPA regarding what constitutes HW, a wider variety of wastes than the USEPA's may be reported as "hazardous."

Installations reported industrial waste sludge generation in a variety of ways. Some report generation when the sludge was actually picked up for disposal, which might be once every other year. Some installations did not report sludge generation, but reported only the end product from the treatment of the sludge, such as spent lime. And some installations that generate industrial sludge do not report it since the State allows small quantity exemption.

Certain States require the liquid waste to be reported as generated volume and weight, but in other states, the sludge is generated in such a small amount that reporting is often not required at all. Since the liquid waste is not disposed of by manifest, but is usually released into the sewer system after heavy metals are removed, there is no record of generation or disposal unless the operator takes the responsibility to log all of the information and send it to the EO for consolidation.

4. What is the relationship between the installation and the DRMO?

Few installations receive a completed copy of the DD 1348-1 they presented to the DRMO or the Defense Reutilization and Marketing Service (DRMS) when a material/waste is turned over. Thus, installation personnel do not know if or when a material is ultimately declared a HW. The hazardous material can be declared as a HW after the DRMO determines that the material can be reutilized, transferred, donated, or sold.

The turn-in and disposal form, DD 1348-1, is an accurate record for transferring materials. However, it does not present an accurate record of wastes being generated and/or treated at an installation because it does not contain all the required reporting information.

Very few installations can present data on HW disposal costs. Installations did not directly fund most of the costs for HW disposal and thus did not keep adequate cost records. Also, the servicing the DRMS did not notify installations of their proportional cost of many of the HW disposal contracts. The DRMO, which often used a single contract that lumped waste disposal services from all of the supported installations, also did not notify the installations. Very few installations could present data on the costs and return of monies from recycling and resell programs since the DRMS provide this information to them only informally.

5. Is the data reported actionable? Can it be related to specific activities and processes that can then be modified to reduce the volumes or toxicity of waste produced?

Some installation HW Management Board were very active and other were not. Lack of command emphasis and support contribute to poor results.

In spite of the Army's efforts to minimize HW generation, the quantities increased continuously in 3 years: 1985-1986 (8 percent) and 1986-1987 (37 percent). This was due more to the increase of *reported quantity than to actual quantity generated*. The 1987 data was most accurate, and the data will become more accurate over time because Army Major Commands (MACOMs) and installations are devoting more resources and attention to HW management. The AEO data was not detailed enough to relate to the specific activities and processes for implementing HW minimization programs.



Problems and Potential Procedural Changes

Problems

Definition of HW Generation Quantity. The AEO message did not clearly define the HW generation quantity; however, the generally accepted definition is the disposal quantity of RCRA Army wastes. The problems revealed by this study were:

- Some state requirements were more stringent than RCRA requirements, and therefore, the state definitions might be different.
- Disposal quantity was not known to the installations because, to maximize RTDS, the DRMO received hazardous items as hazardous materials and not as HW. Also, the DRMO data was not separately maintained by installations.
- One-time generation quantity was included (e.g., spill debris). Therefore, the data did not clearly reflect the annual HW minimization result.
- Treatment/recycle quantity was included as disposal quantity.

Internal Tracking/Manifests. Army policy does not require installations to develop an internal HW tracking system. The two MACOMs interviewed have set no requirement for installations to develop an internal installation HW tracking system, but find that installations that have such systems have more accurate information and reports on HWs.

Disposal. The DOD has mandated that the Defense Logistics Agency (DLA) dispose of HWs for the Army. Once an item is turned in to DRMO, accountability for the item is passed to the DRMO. However, in many cases installations have the custody of the items and regulatory agencies may enforce regulations upon installations, not the DRMO.

All other items turned in to the DRMO must be processed through the RTDS cycle. If items cannot be processed through the cycle, the DRMS may declare them HWs and dispose of them. The DRMS retains accountability for the items. There is no specific procedure for reporting back to the installations the quantities of hazardous materials later declared to be HWs by the DRMS.

The DRMOs do not send a regular report to either the USEPA or the state because regulatory reporting and recordkeeping is the installation Commander's responsibility.

Procurement. A problem common to all of the installation environmental offices was "local procurement." Installation supervisors not aware of the HW problem may unwillingly contribute the problems. Tracking locally procured materials is difficult.

Reporting. Army installations should be aware of minimization reports and regulations and the AEO-requested data should have been consistent with reports previously prepared, or notations should have been made as to why the differences occurred. Regulations are also in place for good recordkeeping, but the Hazmin Status Report indicates that many preparers of the installation responses were not aware of these regulations or did not have the proper documentation to provide the requested information.

Procedural Changes

Internal Tracking/Manifests. It is suggested that installations develop an internal HW tracking system. A standard installation manifest form will help provide required data to the DRMOs, higher headquarters, state agencies, and the USEPA for all waste generated on an installation. The installation manifest could be computerized and made capable to provide required report formats either in hard-copy or electronic form. Implementation of a hazardous material tracking system should also be considered.

Disposal. The DRMO should provide disposal quantity and cost data to installations.

Procurement. A suggestion requiring all supervisors authorized local procurement to sign a statement that the material they are ordering is not a hazardous material has been considered, but not adopted Armywide. Armywide adoption of such a requirement should be reconsidered.

Reporting. More specific definitions of HWs generation quantity should be prepared so that everyone uses the same reporting data definition. Armywide HW data should be categorized as follows:

- RCRA waste disposal quantity (in-house, DRMO)
- Nonrecurring (e.g., spill debris) disposal quantity (in-house, DRMO)
- Non-RCRA (e.g., state unique) waste
- Treatment quantity (RCRA, non-RCRA)
- Recycle quantity (RCRA, non-RCRA).

The Army supply system, installation environmental offices, and the DRMOs respectively use the National Stock Number (NSN), USEPA code, and Contract Line Item Number (CLIN) to identify hazardous materials and wastes. Because there is no correlation among these three systems, it is suggested that the Army develop a reference to correlate NSN, CLIN, and USEPA code.

Regulations and guidance should constantly be updated. Commands should emphasize the need for accurate data collection and reporting.

Command Emphasis. Installations should emphasize the minimization program by placing the personnel and program under a command staff element and ensuring that all senior level personnel are reminded at least quarterly of the requirement to participate.

Monitoring the Progress of the HW Minimization Program. This report has shown that the HW generation baseline data was not reliable. The following method is suggested to analyze the progress of Army HW minimization program:

1. Estimate annual HW minimization quantity based on installation data. Total estimated minimization quantity is a sum of annual minimization quantity for each project since 1985.
2. Compile actual annual HW generation quantity data.
3. Compare the total HW minimization quantity and the actual annual HW generation quantity to indicate the relative progress of HW minimization efforts.

The Congress mandated that the Army reduce HW generation by 10 percent every year from CY88. Therefore, the yearly goals can be stated as a ratio between the total HW minimization quantity and the annual HW generation quantity, which should be 30/70 for CY90, 40/60 for CY91, and 50/50 for

CY92. This relative goal has a greater advantage over a fixed baseline method because Army data is getting more accurate every year.

Conclusions and Recommendations

As a result of record reviews, field interviews, and data analysis, the findings are:

- HW generation quantity data increases (by 8 percent from CY 85 to CY 86, and by 37 percent from CY 86 to CY 87) are due to increases in report quantity, not in actual quantity generated.
- The best records on the amounts of HW generated and disposed of are those reported for 1987. Incomplete and inadequate records for 1985 and 1986 make data from these periods unreliable.
- HW reports that installations currently submit to regulatory agencies can provide HW information to satisfy future data base requirements.

Recommendations for improving HW quantity data and better monitoring the Army HW minimization program are:

- The definition of HW generation quantity should be refined to meet the need of HW minimization program monitoring. It is suggested that generation quantities be divided into RCRA wastes, state-unique wastes, and nonrecurring wastes. Also, treatment and recycling quantities should be included in HW minimization data and newly added HWs.
- The DA and the DLA need to establish a procedure on how the DRMOs are to report back to the installations the amount of materials classified and disposed of as HWs.
- MACOMs and installations must fulfill the requirements to manifest their HWs at the "point of generation" defined by the AEO message, Army Regulations, and 40 CFR, Parts 260-280.
- Army HW minimization progress should be measured by comparing the total HW minimization quantity and the actual annual HW generation quantity.

References

- (1) Army Regulation (AR) 200-1, *Environmental Protection and Enhancement* (Department of the Army [DA], 23 April 1990).
- (2) *Department of Army Hazardous Waste Minimization Program Status Report* (Army Environmental Office [AEO], August 1988)
- (3) Byung J. Kim et al., *Validation of the U.S. Army's Current Hazardous Waste Data*, Technical Report (TR) N-90/10/ADA221242 (U.S. Army Construction Engineering Research Laboratory [USACERL], April 1990).



Acknowledgement

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HAZARDOUS WASTE MINIMIZATION AND TREATMENT OPPORTUNITIES IN THE EIGHTH U.S. ARMY AND THE U.S. ARMY, JAPAN

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82-2-7913-5054

Introduction

The Hazardous and Solid Waste Amendments (HSWA) of 1984 declare hazardous waste reduction to be a national U.S. policy. Hazardous waste (HW) reduction, which is often used as a synonym for hazardous minimization or pollution prevention, is in reality a new approach to environmental management, made necessary because conventional pollution abatement or control technologies simply shift pollutants from one medium to another. In response to this national policy, the Army has established a hazardous waste minimization goal of a 50 percent reduction in the quantity of hazardous wastes generated by 1992, as compared to the baseline calendar year 1985 (AR 200-1).⁽¹⁾

Overseas installations may find it difficult to comply with environmental regulations that do not apply to their unique environmental circumstances. Furthermore, Continental U.S. (CONUS) hazardous waste minimization and treatment technologies may not be applicable to the overseas installations because of the different regulatory, socioeconomic, and technological requirements in the host countries. Also, the limited manpower available to environmental programs in overseas installations, the lack of guidance, and the bureaucracy and communication difficulties common in host country environmental agencies are major problems which impede effective hazardous waste management and minimization programs.

This study is the Army's first attempt to collect and analyze or evaluate the potential for hazardous waste minimization in the Eighth U.S. Army (EUSA) and the U.S. Army, Japan (USARJ).

The objectives of this study were to: (1) assess the hazardous waste management needs of EUSA and USARJ installations, (2) identify, evaluate, and where necessary, adopt responsive hazardous waste minimization technologies, and (3) develop an appropriate technical guidance to help in the adoption and use of these technologies.

Four installations were selected for this study: Camp Carroll and Yongsan Military Reservation in Korea, and Camp Zama and Sagami Depot in Japan. The pertinent host country hazardous waste regulations were collected and compared with U.S. regulations and Army policy.

The U.S. hazardous waste management system was compared with its counterparts in Korea and Japan. The Resource Conservation and Recovery Act (RCRA) definition of hazardous waste is based on characteristics and specific sources of hazardous waste, while Korean and Japanese definitions are based on the type of waste-generating industry, specifically designated hazardous substances, and specific disposal standards and methods. In other words, Korean and Japanese hazardous wastes are defined in



terms of how safely industrial wastes are managed and disposed of. Detail comparison can be found in a U.S. Army Construction Engineering Research Laboratory (USACERL) report.⁽²⁾ A walk-through survey was conducted at four installations and hazardous waste data was compiled based on interviews with operators and facility managers.

Hazardous Waste Minimization and Treatment

The HSWA of 1984 requires hazardous waste generators to certify that, whenever economically practical, programs are in place to reduce the volume and toxicity of hazardous waste. The Office of Technology Assessment (OTA) pointed out that, since pollution control for one medium could mean that waste was merely transferred to another medium, treatment could not be considered as a minimization method.⁽³⁾ Waste minimization should be achieved at the source. However, both the U.S. Environmental Protection Agency (USEPA) and the Army do consider treatment as a minimization alternative.⁽¹⁾⁽⁴⁾ Successful hazardous waste minimization methods include:

- Changed materials purchasing and control methods
- Improved housekeeping
- Changed production or operation methods
- Substitution of less toxic materials
- Reduction in wastewater flow
- Segregation of wastes
- Recycling or reclamation of wastes
- Treatment of waste to reduce volume or toxicity.⁽⁵⁾

Based on the hazardous material and wastes survey data and discussions with EUSA and USARJ hazardous waste managers, the following hazardous waste streams of most concern were identified:

- PCP ammunition boxes: DRMO Sagami used 85 percent of hazardous waste disposal costs for retrograde of the boxes to CONUS in FY87.
- PCB and PCB-contaminated items: United States Forces, Japan has obtained a USEPA waiver for PCB item import ban. Both EUSA and USARJ have difficulty in managing PCB items.
- Waste solvents
- Used oil
- Waste batteries and acids
- Antifreeze

Recommended Hazardous Waste Minimization Technologies for Specific Waste Streams

To meet the RCRA, DOD, and DA requirements, EUSA and USARJ will be able to formulate their own strategies to minimize hazardous waste disposal quantity and disposal expenses. An appropriate hazardous waste minimization strategy is proposed as follows



1. PCP-treated ammunition boxes:

a. Background: EUSA and USARJ have spent millions of dollars to return PCP ammunition boxes to CONUS for disposal. However, a PCP ammunition box has never been hazardous material or hazardous waste, nor is it a hazardous waste by the new USEPA definition. 40 CFR Part 261 (March 1990) defines the regulatory level of PCP as 100 mg/L by the toxicity characteristics leaching procedure (TCLP). USACERL had an Illinois Environmental Protection Agency certified laboratory analyze ammunition boxes that were randomly sampled from EUSA installations. The analysis results ranged from 0.15 mg/l to 1.2 mg/l with median value of 0.52 mg/l. These values clearly proved that the ammunition boxes were not hazardous waste.

The Japanese Waste Disposal and Cleansing Law does not address PCP-treated wood. However, Korean Waste Management Law defines PCP items with 0.003 parts per million (ppm) or more in extracted solution as a special hazardous industrial waste (Article 2. Ministry of Environment Order to Implement the Waste Management Law). This 0.003 mg/L is an unreasonably low limitation compared with 100mg/L in the United States. It appears that the limitation for wastewater effluent was misapplied to PCP-treated wood. The Korean Ministry of Environment (MOE) is presently revising all environmental regulations. This review represents an opportunity to discuss these limitations with the Korean MOE, and to suggest that the MOE revise the limitations based on current scientific evidence.

b. Proposed strategy

(1) Coordinate with the Army appropriate agencies and the appropriate authority will officially acknowledge that PCP ammunition boxes are not hazardous waste. USACERL personnel will be able to provide technical assistance and coordinate the liaison.

(2) DRMO-Bupyong and EUSA will evaluate alternatives to dispose of PCP ammunition boxes as nonhazardous items. Reutilization, transfer, donation and sales (RTDS) by DRMO is a priority consideration.

(3) The following provisions should be made before RTDS activities: An inspection program must be implemented to certify that the ammunition boxes are not contaminated with explosives, that no crystallization is observed on the boxes, and that open burning of wood is prohibited.

(4) Technical Committees will be established to resolve technical questions. Up until now only coordination made was between host country regulatory agencies and U.S. Forces installations. It is recommended that the Technical Committees discuss rational environmental strategies to protect the host country environment and public health based on scientific foundation. USACERL is working through the USFK/EUSA Environmental program Office and the U.S. Embassy in Seoul to establish the Technical Committee.

(5) The senior author of this report has pointed out to Korean Ministry of Environment (MOE) that 0.003 mg/l PCP limitation was an unreasonably low limitation based on scientific data in the United States. MOE officials indicated that they were willing to consider revision of the standard.

2. PCB and PCB-contaminated items:

a. Background: In 1976, the USEPA issued 40 CFR Part 761 to implement the Toxic Substance Control Act (TSCA), prohibiting the manufacture, processing, distribution, and use of PCB items. Two exceptions for continued use were: (1) use in a totally enclosed manner, and (2) use without



presenting an unreasonable risk of injury to health or the environment. The USEPA provided three concentration ranges: PCB-free, which is less than 50 ppm, PCB-contaminated, which contains from 50 to 500 ppm, and PCB, which contains more than 500 ppm.

DLA, DRMS, DRMOs, and the Logistics and the Environmental staff of EUSA and USARJ could not find any solution for the problems of PCB transformers. For more than 10 years, attempts to coordinate hazardous waste management with host countries have met with difficulty. Important unresolved issues include: (1) whether the host country can help with PCB transformer disposal, and (2) how host countries dispose of their own PCB transformers. Commonly, the U.S. Army has been refused such help on the basis that host countries often store spent transformers without treatment, and on the perception that the U.S. Army is better equipped than the host country to handle its own wastes.

It should be noted that Korean and Japanese Governments do not regulate PCB items in the same manner as does the USEPA. In Korea, Article 2 of the MOHSA Order to Implement the Waste Management Law designates PCB concentrated to 0.003 mg/L or more in extracted solution, as a special hazardous industrial waste. This standard is considerably lower than the USEPA's 50 mg/L cutoff. The 0.003 mg/L limit may have been the minimum detection level when the law was written. In fact, the Korean Ministry of Environment does not have any regulation to implement control of PCB transformers. Both Korean Electric Power Corporation (KEPCO) and Korean Office of Environment representatives have reported that they were not aware of any problems in the storage or disposal of PCBs.

A detailed discussion of Japanese PCB regulations can be found in Reference (2). In Japan, the Electrical Equipment Division, Mechanics and Information Industry Bureau, Ministry of Trade and Industry (MTI), Japan, provides a guidance entitled *Concerning Handling of PCB-Containing Electrical Equipment* (September 1984), which includes these guidelines:

- Use of any new electrical system containing PCB is prohibited (Ministry order No.70).
- Users shall store industrial wastes, until disposed of, without hindering conservation of the living environment (Article 12.4, Waste Disposal and Public Cleansing Law).
- Industrial wastes should be stored to prevent spills, groundwater contamination, dispersion into air, and insect breeding (Technical Standards to Store Industrial Wastes).
- Recordkeeping and marking are required (Memorandum of Heavy Industry Bureau and Public Works Bureau).
- A list of 17 PCB item manufacturers and 69 PCB item labels shall be used as references for identification.

Since the Japanese Government identifies PCB transformers by labels, their own PCB transformers contain a PCB concentration of several tens of percent (several hundred thousand ppm). It should be noted that the maximum concentration of USARJ PCB transformers is far less than the Japanese transformers, at 6000 ppm (most contain less than 1000 ppm). USARJ transformers are not labeled according to the Japanese MTI guidance. From a practical and procedural standard, all USARJ PCB transformers should be classified as non-PCB by Japanese criteria.



b. Minimization and treatment technologies

(1) Reuse: The TSCA does not regulate PCB items with a concentration of less than 50 ppm. Therefore, mineral oils with less than 50 ppm PCB concentration can be reused and recycled. However, any waste oil containing any detectable concentration of PCBs cannot be used as a sealant, coating, dust-control agent, pesticide or herbicide carrier, or rust preventative.

(2) Retrofill and reclassification: A PCB transformer is energized allowing PCB leach-out from the core after PCB oil is replaced with a specially prepared PCB-free fluid. The replacement is repeated until the oil PCB concentration becomes less than 50 mg/L. The USEPA requires a 90-day reclassification period after which the transformer may be filled with permanent dielectric fluid. Initial treatment takes about 12 to 24 hours and subsequent treatment requires 8 to 10 hours. Sometimes a processor is attached to the transformer after initial replacement to destroy residual PCB.

(3) Chemical treatment: Many chemical processes have been successfully used to destroy PCBs in dielectric fluids with concentrations up to 10,000 ppm. Those processes also allow reuse of dielectric fluids. The chemical processes attack the PCB molecules at the chlorine-carbon bonds, stripping the chlorine from the biphenyl molecules. The biphenyls are then polymerized to form insoluble sludge.

(4) Incineration: Only high-efficiency incinerators approved by the USEPA may be used to destroy PCBs at concentrations greater than 500 ppm. Incinerators burning PCB liquids must meet the following criteria: 2-second dwell time at 1200 ± 100 °C and 3 percent excess oxygen; or 1.5-second dwell time at 1600 ± 100 °C and 2 percent excess oxygen in the stack gas. Combustion efficiency must be at least 99.9 percent. Once operation conditions have been met, the destruction and removal efficiency must be no less than 99.9999 percent. Commonly available incineration technologies in the U.S. include liquid injection, rotary kiln, multiple hearth, fluidized bed, and co-incineration. Liquid injection systems are widely used because of low capital, operation, and maintenance costs. Disadvantages of this method include clogging of feed nozzles and high sensitivity to waste-heating values. Rotary kiln systems can incinerate several kind of wastes simultaneously, but they are expensive and require skilled operators. Cement kiln systems may also be used to destroy PCBs. However, public and workers' acceptance should be considered. Mobile incinerators for use from a trailer or a ship are also available.⁽⁶⁾

PCBs in concentrations between 50 and 500 ppm may be burned in a high-efficiency boiler. The boiler must meet the following criteria:

- It must be rated at a minimum of 14.6 MW (50 million Btu/h).
- For gas- or oil-fired boilers, CO concentration in the flue gas must be less than 50 ppm.
- For coal-fired boilers, the CO concentration in the stack cannot exceed 100 ppm.
- Excess oxygen must be at least 3 percent.
- The waste cannot exceed 10 percent by volume of the total fuel fed to the boiler.
- Waste can only be fed into the boiler when it is at operating temperature.
- Specific process-monitoring and operating procedures must be followed.⁽⁶⁾

(5) Landfill: Landfilling wastes with concentrations of PCB less than 50 mg/L is not regulated, but hazardous waste landfill is recommended. PCBs in concentrations of more than 500 mg/L may not be landfilled. Landfilling PCBs between 50 and 500 ppm requires USEPA approval with stringent technical provisions to prevent migration and leaching.

(6) Other methods: Innovative treatment methods include microbiological treatment, ultrasonic radiation, plasma system, catalytic oxidation, catalytic hydrogenation, hydrothermal

decomposition, and photodegradation. Detailed discussion of these technologies is beyond the scope of this report.

c. Proposed strategy

(1) Discussion: The concept of PCB management differs among the three nations. The USEPA distinguishes three different concentration categories and prohibits mixing of the three types of waste. The Japanese Government enforces removal of transformers labelled as containing PCBs. The Korean Government does not have implementation regulations for the use of PCB transformers.

At present, the USFJ has obtained a one-time waiver from the USEPA's PCB import ban. However, it should be noted that such waivers are expensive and only stopgap measures.

The Japanese Government does permit an export of the USFJ's PCB transformers with less than 50 mg/L to a third country. However, the USFJ may not wish to export items to a third country for disposal since the action may present a negative image.

It should be noted that the 0.003 mg/L of PCB standard in Japan is based upon limits for wastewater treatment plant effluent, which requires different standards from those for transformers used in an enclosed manner. The limitations on transformers should be different from those for wastewater, and should balance with other hazardous waste limitations, which are based on risk assessment. It appears that the Japanese and Korean standards were based on the detection capability limitation at the time of the enactment of the standards.

Based on a preliminary evaluation above, the most feasible in-country disposal methods are in country incineration, for PCB more than 500 ppm, and use of a high-efficiency boiler, for PCBs with a concentration of 500 ppm or less.

(2) Recommendations: Japanese and Korean PCB regulations should be complied with. New transformers bought from Japanese or Korean manufacturers should be used in a totally enclosed manner. Neither the USEPA nor host governments require subsequent PCB testing for locally manufactured transformers. In-house rebuilding and interior repair of transformers should be prohibited. The DRMO should dispose of unserviceable transformers in accordance with Japanese or Korean procedures. One option is to lease transformers from the Korean or Japanese Government or a Korean or Japanese Company.

Two technical committees (one for Korea and one for Japan) should be formed to establish a strategy for the disposal of existing PCB transformers. Based on the information available, the committees will assess the risk of in-country disposal and make recommendations on the best methods of compliance with host country regulations.

3. Waste Solvents

a. Background: Solvent cleaning and degreasing operations can be categorized as: (1) cold cleaning (solvent application either by brush or dipping), (2) vapor degreasing (used for the high flashpoint chlorinated hydrocarbons such as 1,1,1-trichloroethane or methylene chloride, in the vapor phase, to clean metallic surfaces, and (3) precision cleaning (cleaning of workpieces prior to application of final surface coatings). Solvent has a great recycling potential with little capital and operation costs.



b. Minimization technologies

(1) Segregation: Without segregation, no effective recycling and management of wastes are expected. Especially in EUSA installations, the need for segregation cannot be exaggerated. Before Korean environmental regulations are enforced, the current practice of mixing wastes with slop oil must be stopped.

(2) Substitution: Alternatives to chlorinated solvents include use of alkaline cleaners and high-pressure hot water washer. Flammable petroleum distillate (PD) Type I can be substituted with PD Type II.

(3) Reuse and recycling: High quality solvents once used for precision cleaning can be reused for cleaning other items requiring less purity. Distillation and condensation is a very effective process to recycle solvents.

(4) Process and equipment modification and good housekeeping: small modifications can result in hazardous waste minimization. Techniques include: (1) covering all solvent cleaning units, (2) using refrigerated free board on vapor degreaser units. Randolph (1989) details solvent minimization methods.⁽⁷⁾

c. Proposed strategy: The EUSA has not actively participated in the Army's Used Solvent Elimination (USE) program because DRMR-PAC was able to sell used solvents to a Korean contractor under the slop oil contract. However, it is more economical for EUSA to recycle solvents. Furthermore, when Korean Environmental regulations are more stringently enforced, the EUSA will have to pay a disposal fee. Also, since it is more economical to recover solvent on site, it may be a good opportunity for the EUSA to start a solvent recovery program. Recommended locations for solvent recovery are the consolidated points for Camp Carroll (Bldg 327 [Major Assembly Plant]; Bldg 405 [Direct Support Maintenance]; and Bldg 658 [Tactical Vehicle Maintenance]), and the consolidated point for vehicle maintenance facilities in Camp Coiner Yongsan, Seoul.

4. Waste oil

a. Background: Waste oil refers to lubricating oils that have gone through their intended use cycle. In EUSA, used oil is released to Korean contractors under a sales contract. In the USARJ, Camp Zama and Sagami Depot turn in used oil to Hakozaki Terminal. The terminal often cannot accept the used oil because of limited capacity.

b. Minimization and treatment:

(1) Combustion: 40 CFR part 266, subpart E, defines regulations for used oil burned for energy recovery.

Used-oil space heaters are considered to be a reasonably efficient means of disposing of waste oil generated on site. The USEPA has provided a conditioned exemption from the prohibition of burning of off-specification fuels in used oil space heaters. The referenced conditions are: (1) that the heater burn the oil generated by the facility, (2) that the heater be designed with a maximum capacity of not more than 0.5 Mbtu/h, and (3) that the combustion gases vent to the ambient air.

(2) Re-refining: Currently available technologies have the capability to yield a recycled oil product with characteristics comparable to virgin lube oil. Refiners are currently not operating at system capacity due to the expense of refining costs and the demand for waste oil as fuel.

b. Proposed strategy:

(1) The experience at Camp Humphrey showed that a Korea-wide waste oil collection may not be economical. However, small systems that burn near the waste oil generation site will be economical.

(2) Waste oil should be used as fuel within the installation that generates the waste. Used-oil space heaters will be provided at several locations for demonstration purposes.

5. Waste batteries and antifreeze solution

a. Background: The USEPA has reported a proved concept for recycling battery acids.⁽⁸⁾ Although commercial systems for recycling antifreeze are available, none are currently used on either EUSA or USARJ installations. In the absence of an antifreeze recycling systems, after coordination with the Utilities Division or the Sanitation Branch Chief, antifreeze solution may be discharged into a sewer system instead of being collected into a used-solvent containers.

b. Recommendations:

(1) Antifreeze should be discharged into the sewer system until an antifreeze recycling system becomes available.

(2) Battery acid recycling should also be considered.

Conclusions

1. PCP ammunition boxes should be considered as nonhazardous material. USACERL should be tasked to coordinate a liaison with the appropriate Army organizations to draw a consensus on this concept and to declare the Army position on PCP ammunition boxes.

2. Technical committees should be formed to evaluate in-country disposal of existing PCB items in EUSA and USARJ, to recommend the best available disposal methods that comply with host country standards, and also to resolve the PCP problem.

3. Solvent recovery systems should be used.

4. Burning of used oil in custom-made space heaters should be tested and demonstrated in EUSA and USARJ installations.

5. Spent antifreeze should be reclaimed.

6. As of June 1991, USACERL is working with USFK/EUSA Environmental Program Office to demonstrate solvent recovery, antifreeze recovery, and used oil burners at EUSA installations. When such hazardous waste minimization program is fully implemented, an approximately 80 percent reduction of hazardous waste generation quantity is expected.

References

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WET AIR OXIDATION OF TNT RED WATER

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ABSTRACT

Treatment of TNT red water by wet air oxidation results in a decrease in COD, TOC and other specific chemical compounds such as 2,4-DNT-3- and 2,4-DNT-5-sulfonates. The oxidation temperature and initial oxygen pressure control the degree of treatment. Partially treated red water may be added to an activated sludge wastewater treatment system without adversely affecting COD removal.

INTRODUCTION

The production of the explosive TNT (trinitrotoluene) involves the successive nitration of toluene in nitric and sulfuric acid:

toluene -> nitrotoluene -> dinitrotoluene -> trinitrotoluene
(raw TNT)

The selectivity of the nitration reactions results in the synthesis of about 95.5% α -TNT (2,4,6-trinitrotoluene) and the remaining products consisting of various unsymmetrical TNT isomers and other modified aromatic compounds. This raw TNT does not meet the standards required for the explosive--only the α -TNT is desired. Consequently, a purification process is carried out in which sodium sulfite is reacted with the raw TNT mixture. The sulfite reacts selectively with the unsymmetrical TNT isomers producing sulfonated dinitrotoluenes (DNT) and other sulfonated organic compounds. The slightly soluble α -TNT is easily separated from the solution of soluble sulfonated compounds for explosive uses.

The remaining solution containing the sulfonated DNT has a characteristic dark red color and is hence called red water. It is a listed hazardous waste by the EPA. Several projects have been initiated to recover valuable materials present in red water with little success. Additionally, red water is not efficiently treated by common wastewater treatment processes. Schott et al. (1943) have shown that precipitation, activated carbon

adsorption, ozonation, fractional distillation and biological treatment are all ineffective for red water treatment. At the present time, the only practical disposal method is to transport the concentrated red water to an appropriate site for incineration, a costly and complex endeavor. Consequently, no TNT is currently being produced in the U.S., partially due to the red water disposal problem.

A recent study on red water disposal options (PEI Associates, 1990) has listed wet air oxidation (WAO) as one of four promising technologies (the other three being incineration processes). WAO is a treatment process under high pressures (1500-2000 psi) and temperatures (200-350 °C) in the presence of oxygen. The harsh conditions initiate radical reactions that result in the oxidation of aqueous contaminants. Final products depend upon the reaction conditions; under the harshest conditions carbon dioxide and simple mineral acids result. Recently, several investigations have been performed examining the WAO of hazardous aqueous wastes (Baillod et al., 1979; Joglekar et al., 1991). Results have shown greater than 99.9% removal of substituted phenols with corresponding COD reductions greater than 90% (Joglekar et al., 1991). Consequently, a thorough examination of the WAO of red water is warranted.

MATERIALS AND METHODS

Actual red water was obtained from ICI Canada. The red water was filtered through cotton to remove suspended solids and refrigerated (4 °C). For preliminary work, mostly as a safety precaution, working red water solutions were diluted 1:100 using deionized water.

The WAO apparatus was supplied by PARR Instrument Co. It consists of a 2-L stainless steel reaction vessel enclosed by a heating element. Temperatures up to 350 °C and pressures up to 2500 psi are possible. A variable speed magnetic stirrer provides mixing and an auxiliary gas vessel allows strict control over an initial purge of oxygen to the reactor.

The reactor was charged with 1 L of the diluted red water and excess oxygen (based on initial COD). Operating pressure, P_t , was estimated by the summation of the water vapor pressure at the operating temperature, P_{vap} , and the pressure of the initial oxygen charge, P_{O_2} , corrected to the operating temperature. For this work, an actual reaction time of 1 hour was used; however this does not include the time to reach operating conditions (approx. 20 min) and a cool-down period (approx. 10 min).

Nitrite, nitrate, sulfite, sulfate and acetic acid were quantified on a DIONEX Model 2020i ion chromatograph. A conductivity detector was used along with a Hewlett Packard Model 3396A integrator. A HPIC-AS4A column and a HPIC-AG4A guard column were used for the inorganic ions. The eluent was 0.0028 M

NaHCO_3 + 0.0022 M Na_2CO_3 at a flow rate of 2 mL/min. For the acetic acid analysis, a HPIC-AS1 column and a HPIC-AG1 guard column were used. In this case the eluent was 0.005 M sodium borate at 2 mL/min.

Gas chromatography (Hewlett Packard GC Model 5890) was used to measure the non-polar organic compounds. An 8 meter capillary column was used with an ECD. The oven temperature was initially at 128 °C and ramped to 220 °C at 20 °C/min. The injection temperature was 270 °C. Toluene was used to extract the non-polar organics from the aqueous phase and was directly injected (2 μL) onto the column.

The DNT sulfonates were measured using reverse phase ion-pairing liquid chromatography (DIONEX). In this case the analytical column was a MPIC-NS1 and the guard column a MPIC-NG1. The eluent was 28% acetonitrile and 2 mM tetrabutylammonium hydroxide. The flow rate was 1 mL/min and a conductivity detector was used. Details on the development of this method for DNT sulfonates are provided elsewhere (Hao and Phull, 1991).

TOC and COD were measured using an O.I. TOC analyzer Model 700 and by the dichromate reflux method (Standard Methods, 1985), respectively. Total solids was determined by heating a sample of the solution at 103 °C, fixed solids under 500 °C combustion. Volatile solids was determined by difference.

An activated sludge batch system was used to evaluate the effects of partially treated red water on COD removal capability. The sludge seed was taken from a local treatment plant. A 50 mL concentrated sludge sample was diluted to 500 mL using deionized water plus a fraction of the treated red water that had been adjusted to pH 7. This system was supplemented with a glucose substrate and samples were taken periodically for COD analysis.

WAO RESULTS

WAO experiments were conducted at three different initial oxygen pressures (although the P_{O_2} at the working temperatures were different) and several temperatures to determine optimum conditions for red water treatment. Results are presented in Table I. The experiments were conducted during an eight-month period which resulted in slightly different raw red water characteristics. It was obvious that chemical transformations took place in the red water as a result of WAO as the color the water was altered by the treatment. Under conditions of low temperature and oxygen pressure, the effluent was a dark yellow color; under the more harsh oxidation conditions, the solution was a lighter yellow to essentially clear.

Table I. Characteristics of WAO Treated Red Water.

Parameter	Raw Red Water	Run Number							
		1	2	3	4	5	6	7	8
P _{O2} @ 25 °C		19	19	19	90	90	90	380	380
Set Temp (°C)		200	260	320	200	260	320	225	300
P _{O2} @ Set temp.		30	34	38	143	161	179	635	730
P _T		255	714	1676	368	841	1817	1005	1980
pH	7.12 7.10 7.6	5.10	4.46	5.64	3.37	3.27	3.05	3.1	2.8
Acetic Acid (mg/L)	0	12.5	49.5	44.2	30.7	60.3	37.5	54	54
COD (mg/L)	816 800 685	418	118	18	280	72	7.6	114	8
TOC (mg/L)	464 495 544	294	150	35	255	112	30	80	42
UV absorbance									
200 nm	1.25	0.88	0.46	0.26					
432 nm	0.127	0.034	0.008	0.002					

Table I (cont.). Characteristics of WAO Treated Red Water.

Parameter	Raw Red Water	Run Number							
		1	2	3	4	5	6	7	8
2,4-DNT-3-sulfonate	-	99	77	0	83	64	0	33	0
2,4-DNT-5-sulfonate	-	78	0	0	72	0	0	5	0
SO ₄ ²⁻ (mg/L)	369	999	1163	1243	1001	1160	1208	940	1109
SO ₃ ²⁻ (mg/L)	35	0	0	0	0	0	0	0	0
NO ₃ ⁻ (mg/L)	13	129	202	198	230	271	335	131	339
NO ₂ ⁻ (mg/L)	229	0	0	0	0	0	0	0	0
TS (mg/L)	3087 3147 2840	2647	2087	1893	2420	1987	1973	2045	1820
TVS (mg/L)	1353 1347 1020	1007	440	160	794	393	127	340	70
(% of TS)	36-44	38	21	9	33	20	7	17	4

* as % of raw red water since reliable analytic standards for DNT sulfonates are not available.

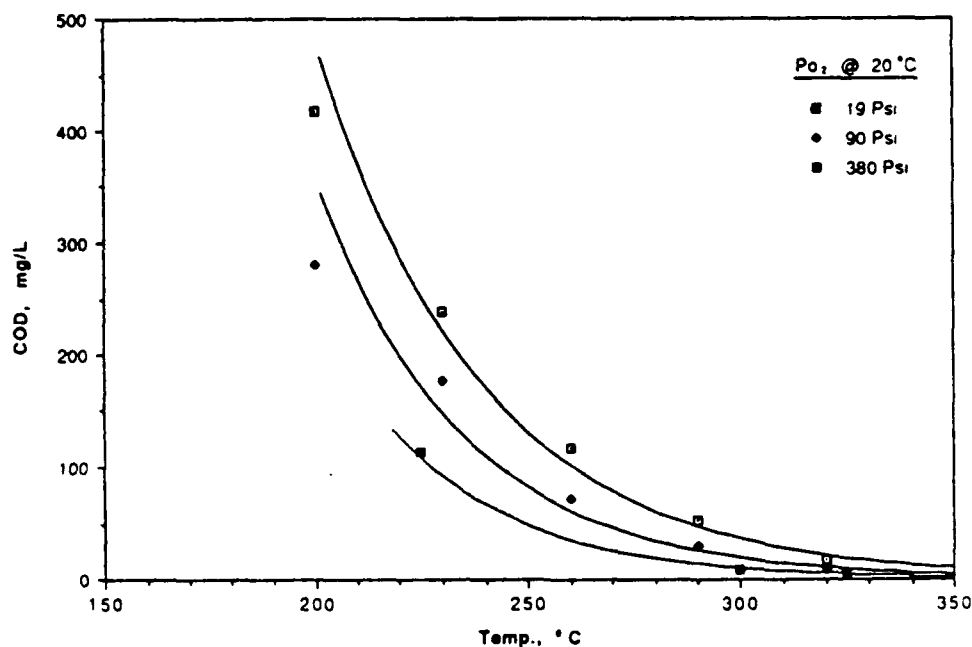


Figure 1. COD in WAO Treated Red Water as a Function of Temperature at Three Initial Oxygen Pressures.

COD and TOC

Both the COD and TOC are reduced significantly after the WAO treatment of the red water. Figure 1 shows the remaining COD as a function of temperature at different initial oxygen pressures. COD removal is much greater at the higher temperatures and approaches 99% at temperatures above 300 °C. TOC data follow the same trends. Thus the reduction in oxidizable organics in the red water is evident. Additionally, light absorbance of the treated red water is less than that of the raw water, decreasing with increasing temperature (Table I). This is also an indication of the oxidation and destruction of aromatic compounds in the wastewater.



Solids

Fixed solids remained approximately constant regardless of the WAO treatment conditions. However, volatile solids decreased as temperature and P_{O_2} increased, reducing to less than 10%, again confirming the oxidation of organic material.

DNT Sulfonates

Concentrations of both DNT sulfonates decreased as a result of WAO. The reduction of these DNT sulfonates was related to both temperature and oxygen pressure. For example, 67% and 95% reductions were achieved for 2,4-DNT-3-sulfonate and 2,4-DNT-5-sulfonate, respectively, for run #7 (225 °C, 380 psi O_2). Both compounds were undetectable after treatment at 300 °C. Large increases in inorganic sulfate were found, indicating oxidation of the sulfite group from the DNT sulfonate. Analysis of raw and treated red water samples indicate that as temperature increases, the concentrations of measured nitroaromatics other than α -TNT (i.e., NB, DNTs, DNB and TNB) initially increase, and subsequently decrease at higher temperatures and oxygen pressures. Also an increase in NO_3^- was noted, suggesting removal of some nitrogen groups from organic compounds.

Acetic Acid

Acetic acid was not present in the raw red water. However it was detected after treatment by WAO. Acetic acid has been commonly found in WAO treatments of other compounds (Foussard et al., 1989) and is an intermediate in the oxidation of many organic compounds to carbon dioxide. The accumulation of acetic acid is highest at lower temperature and lower oxygen pressure. Under these conditions, oxidation of the original organic materials in the red water commences producing organic acids. However harsher conditions are required to further enhance the oxidation of the acetic acid and the remaining concentrations are lower at high temperatures.

pH

The WAO process causes a decrease in the solution pH. The final pH was 4.5-5.6 under the lowest oxygen pressures but was as low as 2.8 under the highest oxygen condition. The pH decreases due to the formation of mineral acids during the oxidation process. As the oxidation becomes more complete at the higher pressures of oxygen, more acids are formed.

EFFECT OF WAO TREATED RED WATER ON BIOLOGICAL SYSTEMS

Figure 2 shows the biological removal of COD in five seeded activated sludge samples. The solutions ranged from 0 to 75% treated red water (320 °C and 90 psi P_{O_2} ; pH adjusted to 7). The



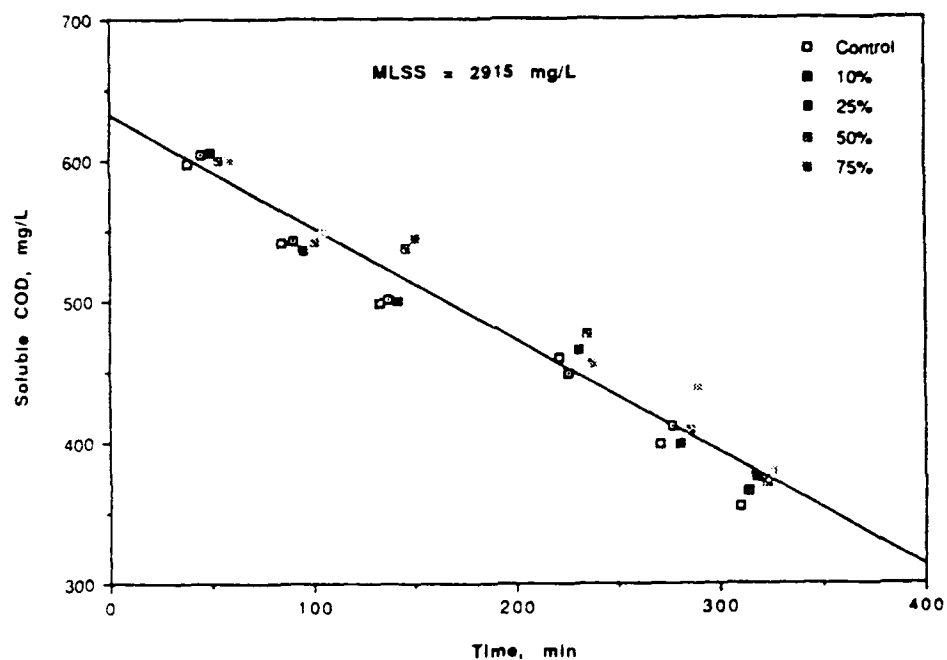


Figure 2. Effect of WAO Treated Red Water on COD Removal Kinetics in Laboratory Activated Sludge System. Numbers Equal % Makeup of Treated Red Water.

COD removal efficiency is essentially identical in all five mixtures. Thus the treated red water did not produce a toxic effect on this biological treatment system.

DISCUSSION

Wet air oxidation is a very promising process for red water treatment. Under extreme conditions, i.e., high temperature and oxygen pressure, apparently all of the organic materials in the diluted red water are completely oxidized. This is demonstrated by decreases in COD, TOC and volatile solids as well as a drastic change in solution color. Concentrations of α -TNT, 1,3,5-trinitrobenzene, 2,4-DNT-3-sulfonate and 2,4-DNT-5-sulfonate are significantly reduced with a concurrent increase in inorganic

sulfate and a slight increase in nitrate. Under less harsh conditions, removals of these parameters are less. However partial oxidation is evident, which may result in a decrease in the toxicity of the treated red water. Acetic acid, an intermediate commonly found in oxidation processes, is detected under low temperature/pressure conditions. An initial experiment has shown that up to 75% addition of partially treated red water may be added to an activated sludge system without affecting the COD removal capabilities.

Therefore it may be possible to partially treat the red water using WAO to oxidize some of the toxic materials under relatively low temperatures and pressure. The effluent, which may contain oxidized organics such as organic acids (i.e. acetic) would at this point be biodegradable and biologically non-toxic, allowing further treatment in a conventional activated sludge system after pH adjustment. Work on examining the treatment of the red water, including kinetics of organic removal as well as the biological treatment of partially treated red water is currently being performed.

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REGIONAL GROUNDWATER FLOW MODEL AT ROCKY MOUNTAIN ARSENAL

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A finite element numerical model of regional groundwater flow at Rocky Mountain Arsenal (RMA) was developed using a proprietary finite element code. The regional model study area encompasses RMA and extends considerable distances north and south of RMA. The boundaries of the study area are aligned with four major surface waterways. The model simulates steady-state, two-dimensional areal flow in an unconfined flow system that comprises shallow alluvium and upper Denver Formation materials where the alluvium is unsaturated. The regional flow field is affected by interactions with surface-water bodies, recharge from irrigation and precipitation and other sources, regional updip flow along bedding planes in the Denver Formation, groundwater pumping, and underflows. Calibration of the model was based primarily on mean water-table elevations for 1981 through 1987. The regional model is intended to provide a current, comprehensive tool for analyzing and predicting area-wide groundwater movement. The model provides a numerical framework that can be used to address questions regarding shallow groundwater flow in and around RMA, including the effects of stresses on hydraulic potential, flow direction, and flow magnitude. The model can be used to analyze flow rates, travel times, and rates of surface-water losses and gains. It was anticipated that the regional model would be used to determine reasonable boundary flows for possible future local models of groundwater flow and contaminant transport.

INTRODUCTION

A numerical model of regional groundwater flow at Rocky Mountain Arsenal (RMA) was developed that simulates steady-state, two-dimensional areal flow in an unconfined groundwater flow system (UFS). The model accounts for many of the hydrologic processes occurring at RMA and illustrates the importance of groundwater-surface-water exchange for the numerous surface-water bodies in and around RMA.

Groundwater flow and contaminant transport models previously developed for RMA have been confined to local sites within and around RMA boundaries, or to regions that do not fully envelop RMA and the areas that influence its hydrology. Models that have been prepared on a regional scale, other than this model, either have not yet been made public or were developed before the

availability of recently collected hydrogeologic data and interpretations. During the 1980s, considerable hydrogeologic data were collected from in and around RMA. Analyses of these data have been used to characterize many of the groundwater flow processes in the region and the hydrogeologic influences on them. Using these data, this regional model is intended to provide a current, comprehensive tool for analyzing and predicting area-wide groundwater movement in and around RMA.

This paper is a description of the procedures and approach used in the development of the regional model. This paper also describes the model input and calibration procedures. Finally, the model results are discussed and summarized.

PURPOSE OF REGIONAL MODELING

The purpose of regional modeling is as follows:

1. To provide a current, comprehensive tool for analyzing and predicting area-wide groundwater movement, including flow direction, flow magnitude, and the degree to which various hydrogeologic factors and stresses affect hydraulic potential.
2. To provide a numerical framework for quantification of pertinent hydraulic parameters, including flow rates, travel times, and surface water gains and losses.

The regional model is part of what was intended to be an organized set of models for assessing groundwater quality remedial actions at RMA. It was anticipated that the area encompassed by the regional model would be divided into subregions for which more detailed contaminant transport models could be prepared. For numerical simulation reasons, subregional transport models are typically developed using grids or meshes that are more refined than those used in a regional-scale model. However, results of the coarser regional model can often be incorporated into the local models in the form of boundary

conditions or calibrated hydraulic parameters (Duffield and others, 1987). This technique of using both regional and subregional models preserves important effects of regional flow phenomena in the subregional models and permits a cost-effective and accurate treatment of transport modeling at contaminated sites.

DESCRIPTION OF THE STUDY AREA

RMA is located in Commerce City near Denver, Colorado (Figure 1). The area included in the regional flow model is shown in Figure 2. This area, which covers approximately 87 square miles, encompasses RMA and extends several miles north and south of RMA. The boundaries of the study area coincide with four surface waterways: South Platte River, Sand Creek, Second Creek, and the Highline Canal.

Subsurface movement of water in the study area is quite complex. Most groundwater flow occurs within shallow alluvial and eolian deposits. For convenience, the alluvial and eolian deposits are simply referred to as "alluvium" in this paper. Underlying the alluvium is the Denver Formation (Denver Fm) of Late Cretaceous and Tertiary age,

which generally consists of indurated sedimentary deposits and is commonly less permeable than the alluvium; however, subsurface water does appear to move through the Denver Fm (May and others, 1982; Ebasco and others, 1989). In many parts of the study area, the alluvium is unsaturated. In such parts, the top of the saturated zone is located in the upper portions of the Denver Fm.

RMA and the groundwater-bearing geologic units underlying it are part of a larger system called the Denver Basin, an

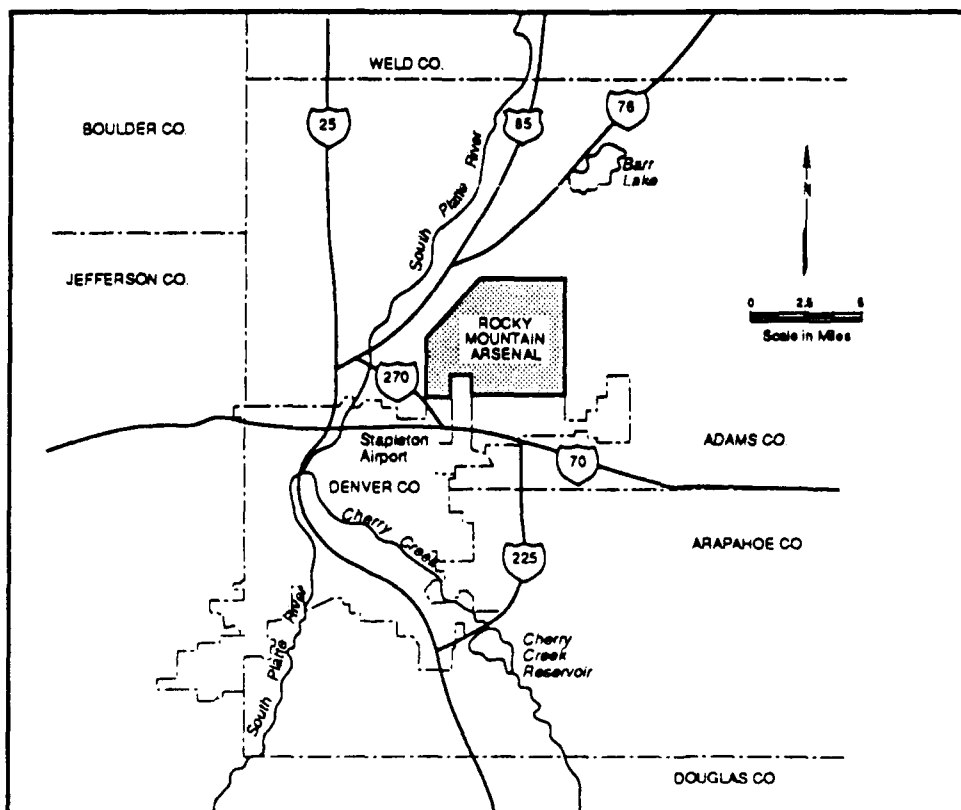


Figure 1: Location Map

oval-shaped structural basin covering approximately 6700 square miles. The Denver Basin consists of five separate bedrock formations (Robson and Romero, 1981): the Fox Hills Sandstone, the Laramie and Arapahoe Formations of Late Cretaceous age, the Denver Fm, and the Dawson Arkose of Tertiary age. Of these five formations, only the Denver Fm and, to a very minor extent, the Arapahoe Formation appear to be in direct hydraulic connection with the shallow alluvium in the study area.

Numerous natural and manmade surface-water bodies are located in the region, including the four selected as boundaries of the study area (Figure 2). Interaction between the groundwater and the many streams and canals significantly influences groundwater flow. Within RMA, infiltration from lakes, ponds, and, to a lesser extent, basins (Figure 3) also influences groundwater levels.

CONCEPTUAL MODEL

Regional groundwater flow at RMA is conceptualized and modeled as two-dimensional areal flow that occurs within a shallow unconfined flow system consisting of both alluvium and portions of the upper Denver Fm. The regional flow field is affected by the following components:

- Groundwater-surface-water exchange
- Recharge from irrigation, precipitation, and other sources
- Updip flow from the Denver Fm
- Groundwater pumping
- Boundary underflows

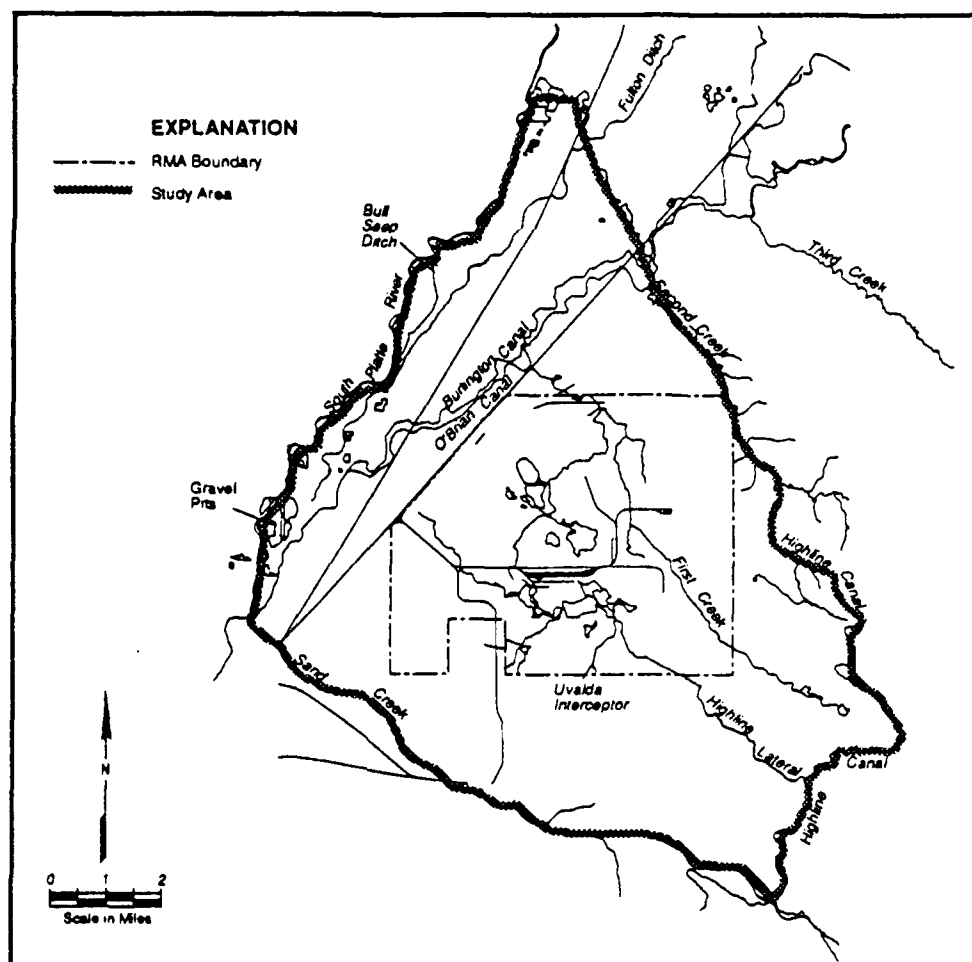


Figure 2: Study Area

These components of the conceptual model are summarized in Figure 4 and described in the following sections.

Unconfined Flow System

The uppermost water-bearing unit at RMA is unconsolidated alluvium. The alluvium comprises deposits of Quaternary age and consists of alluvial fill, eolian sand and silts, glacial outwash, fluvial sands, gravels, silts, and clays (Ebasco and others, 1989). The thickness of the alluvium is variable, ranging from 0 to 130 feet within the model study area. Areas of thicker alluvium are commonly associated with numerous paleochannels that traverse the region, and with terraces of the South Platte River. The thicker alluvial sequences are commonly attributed to erosion into the underlying bedrock and subsequent deposition of fluvial sediments by the streams and rivers that once existed in these areas (Morrison-Knudsen Engineers, Inc. [MKE], 1988). The



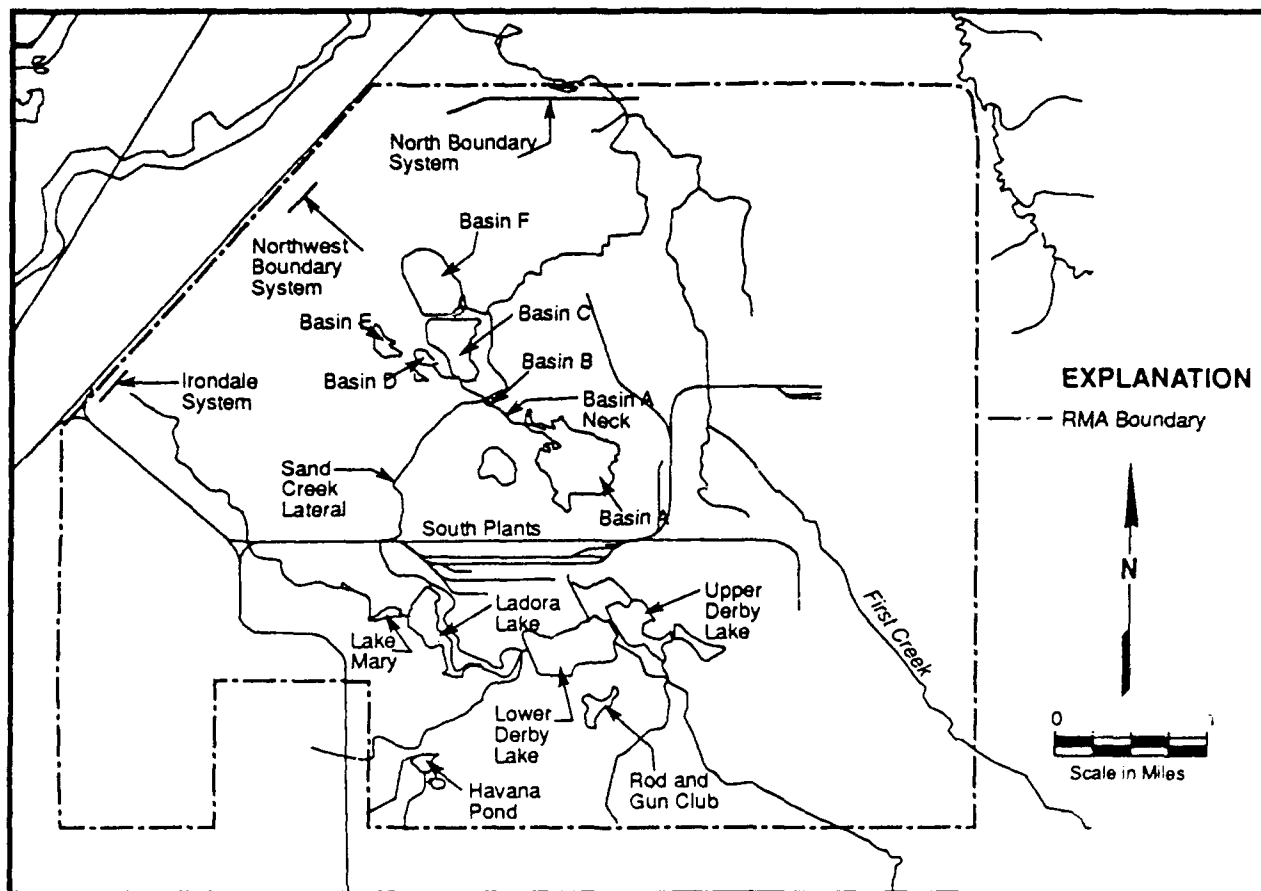


Figure 3: Lakes and Basins at RMA

alluvial materials in the paleochannels and river terrace areas are also generally more coarse-grained and permeable than in interfluvial zones, primarily because the flows in the ancient streams were of sufficient magnitude to transport and deposit such coarse-grained materials (MKE, 1988).

Underlying the alluvium over most of the study area is the Denver Fm of late Cretaceous and Tertiary age. The deposits in the Denver Fm are largely indurated and, as a consequence, are usually characterized by lower hydraulic conductivities than those determined for the alluvium. The Denver Fm consists of alternating sandstones and shales, siltstones, claystones, low-grade coal, and lignite (May, 1982; Ebasco and others, 1989). In this paper, the Denver Fm is referred to as bedrock, and the interface between the alluvium and the Denver Fm is called the bedrock surface. As previously stated, much of the shallow groundwater occurs in saturated alluvium. At many sites, the local hydraulic head lies below the bedrock surface and the alluvium is unsaturated; in these latter areas it is assumed that the

base of the groundwater flow system is different than the bedrock surface.

Most groundwater moving through the study area does so under unconfined conditions within the alluvium. However, because of evidence that some groundwater moves through the Denver Fm (May, 1982; Ebasco and others, 1989), it is assumed in the conceptual model that shallow groundwater flow occurs within a single unconfined flow system that consists of both saturated alluvium and the upper Denver Fm in areas where the alluvium is unsaturated (Figure 5). According to this concept, the continuous UFS covers the entire study area. Within the UFS, groundwater moves generally from southeast to northwest.

The regional flow model in this study area is based primarily on time-averaged conditions for 1981 through 1987. Independent analyses (Ebasco and others, 1989) suggest that no major declines or increases in regional groundwater levels occurred during the 1980s. Seasonal and short-term variations in groundwater levels and the processes affecting them do occur, yet the

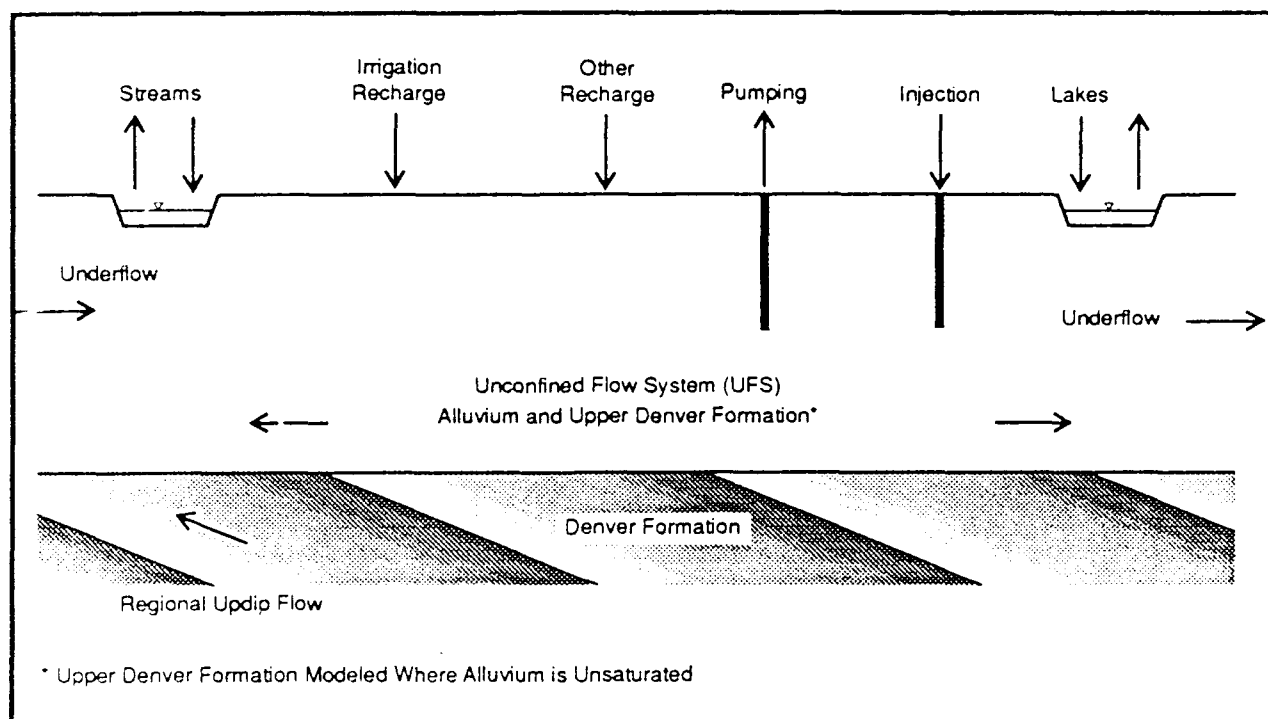


Figure 4: Conceptual Model of Regional Groundwater Flow

average behavior of these variables during the past several years is relatively constant. Consequently, the groundwater flow system in the study area is described as recently existing in a state of dynamic equilibrium (Freeze, 1969), and the regional model is herein referred to as a steady-state model. The assumption of steady-state flow conditions was also made in previous models of the RMA area (e.g., Konikow, 1977).

Groundwater Surface-Water Exchange

The many surface-water bodies in this study area have a significant effect on flow in the UFS. Infiltration losses from many of the streams and canals in the region contribute substantial amounts of flow to the groundwater domain. The most significant surface-water body that receives groundwater discharge is the South Platte River. Along nearly all the South Platte River length in the study area, groundwater appears to be moving toward the river from both north and south (Konikow, 1975). Conversely, parts of First Creek and Second Creek (Figure 2) appear to be gaining in some locales and losing in others. It should be noted that the relative direction of flow between local streams and the UFS can vary with time, especially seasonally. Despite such temporal variations, it is assumed in this paper that the

long-term, average stream-aquifer exchange (gaining or losing) along specific stretches of the waterways can be estimated, using available data on stream and canal flows, streambed data, and groundwater levels. Most irrigation canals have the potential to lose water because water surfaces in canals are typically higher than ambient water-table levels.

The lakes and ponds in the region can also be classified as gaining or losing, e.g., studies suggest that the Derby Lakes (Upper and Lower) tend to lose water, whereas Ladora Lake and Lake Mary (Figure 3) experience net annual gains (MKE, 1987; Ebasco and others, 1989).

Recharge From Irrigation, Precipitation, and Other Sources

Recharge from the application of irrigation water occurs primarily in a strip of land underlain by South Platte River terrace deposits that are located north and northwest of RMA along the south banks of the river. Although most of the irrigation water is derived from annual river diversions to irrigation canals in the region, approximately 8 percent (Konikow, 1977) is also taken from irrigation wells. This study follows the approach of Konikow (1977) and MKE (1987) and assumes that approximately 45 percent of the

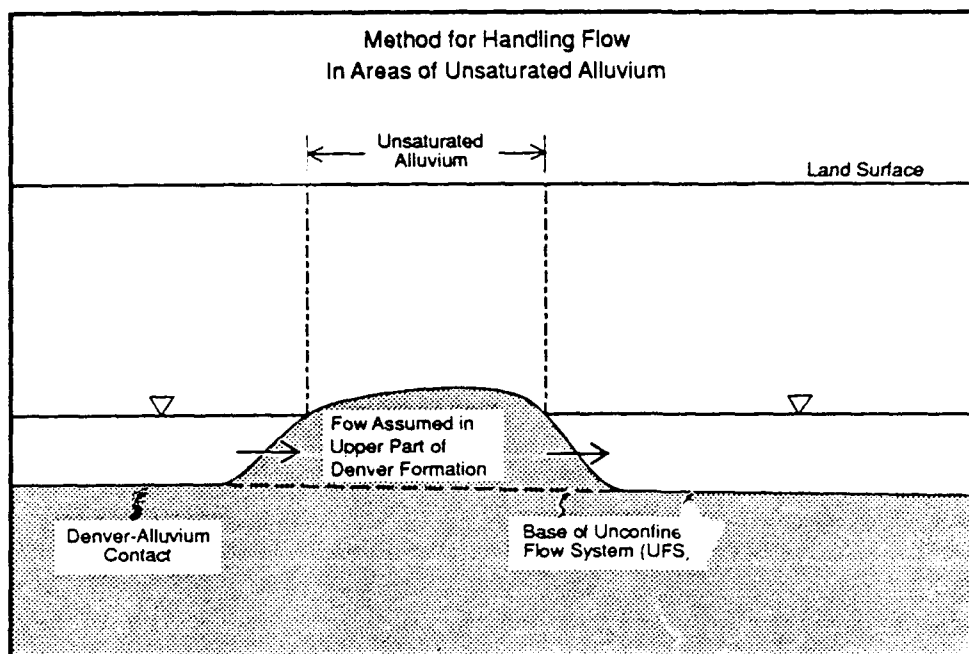


Figure 5: Definition of the Unconfined Flow System

applied water ultimately recharges the UFS.

A considerable amount of recharge is also derived from sources other than irrigation. Other potential sources of areal recharge include (1) infiltration of precipitation, (2) lawn watering in residential areas, (3) leaky sewers (storm and sanitary), (4) runoff in commercial/industrial areas, (5) leakage from basins A, B, C, D, E, and F, and (6) recharge in the South Plants area. Although the amounts of recharge from these sources cannot be precisely determined, the likely locations and quantities of recharge were estimated using previous studies.

Updip Flow From the Denver Formation

Hydraulic interactions between the UFS and the underlying bedrock have potential bearing on the regional model because flow within the UFS may be affected by such interactions. Inspection of maps (Ebasco and others, 1989; MKE, 1989) delineating subcrop areas for bedrock units underlying RMA and surrounding areas shows the Denver Fm subcrops over most of the study area, whereas the Arapahoe Formation subcrops only in a small area near the South Platte River. Because groundwater flow within the UFS in the South Platte River area is relatively large, and flows through the bedrock units are relatively minor, it is unlikely that the Arapahoe Formation has a strong influence on flow simulated by the regional model.

In comparison, permeable materials within the Denver Fm are known to subcrop in parts of RMA where UFS flows are relatively small and are notably influenced by even small gains or losses. As a result of these findings, only the Denver Fm has been considered when attempting to incorporate the effects of UFS-bed-rock interactions into the regional model.

The stratigraphic sequences of the Denver Fm dip regionally at about 1 degree to the southeast (Ebasco and others, 1989) and the base of the UFS shows an average slope of about 0.3 degree to the northwest. As a result, the Denver Fm *subcrops unconformably* against the base of the UFS. Descriptions of Denver Fm geology (Ebasco and others, 1989) indicate the Denver Fm can be separated into distinct hydrogeologic units (HGUs). Furthermore, the strata can be separated into aquifer HGUs (in which sandstone and/or lignite are predominant) and aquitard HGUs (composed by mostly, but not exclusively, fine-grained materials). Because the permeability contrasts between the sand aquifer zones and fine-grained aquitard zones can be as much as several orders of magnitude, flow in the aquifers is predominantly parallel to bedding (nearly horizontal), whereas flow perpendicular to bedding (essentially vertical) is expected to be common in the aquitards. However, lateral discontinuities within aquifer HGUs can cause vertical flow to occur in layers where horizontal flow would otherwise predominate. Similarly, nearly horizontal lenses and stringers of sand found in aquitard HGUs can help induce local flow parallel to bedding planes in aquitard units that may be dominated by vertical water seepage.

Earlier studies (Robson and Romero, 1981) and examination of hydraulic heads in the aquifer HGUs of the Denver Fm (May, 1982; Ebasco and others, 1989) suggest that, on a regional scale,



most groundwater in the Denver Fm generally moves updip to the northwest. The source of this water is recharge from deep infiltration of precipitation in highland areas of the Denver Basin located south of RMA (Robson and Romero, 1981).

Because of the predominance of updip flow in the Denver Fm, and difficulties associated with estimating vertically downward flows across the alluvium bedrock contact, it is assumed that all parts of the UFS within the study area receive net groundwater inflow from the Denver Fm. The adopted approach (Figure 6) assumes that aquifer HGUs contribute more water to the UFS than do aquitard HGUs.

Groundwater Pumping

Spatially variable estimates of groundwater pumping for irrigation purposes are difficult to make because detailed pumping data for the numerous irrigation wells in the area do not exist. To account for this component in the regional flow model, a previous estimate by Konikow (1977) of

a uniform, per-well groundwater withdrawal rate is used. This unit rate is applied to each of 103 irrigation wells in the model area.

Significant groundwater withdrawal occurs from nine municipal supply wells located west of RMA and owned by the South Adams County Water and Sanitation District. The pumping rates for these wells were estimated using data from previous studies.

Pumping from domestic wells was ignored in the regional model, primarily because domestic well locations are largely unknown.

Boundary Flows

The model boundaries, in addition to being areas where water exchange occurs between the UFS and the four surface waterways surrounding the model, are also affected by boundary underflows. To account for inflow to the UFS from boundary underflow, specified flux boundary conditions are used.

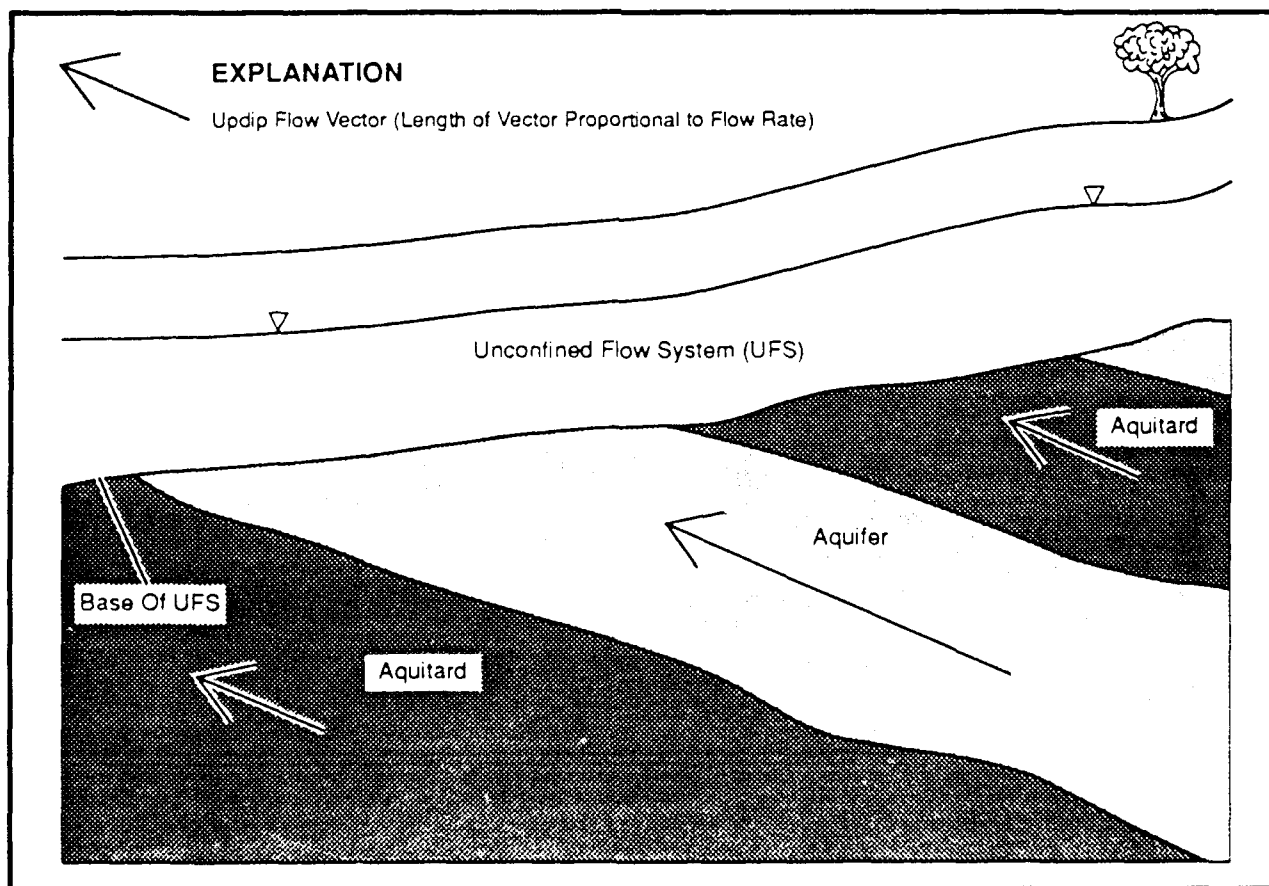


Figure 6: Conceptual Model of Flow in the Denver Formation

NUMERICAL MODEL

The regional modeling was performed using ATLAS-SOLUTE, a proprietary, finite element code (HLA, 1988). This code is capable of simulating fluid flow and solute transport in both saturated and unsaturated porous media.

The regional flow model area was discretized using a mesh of 1800 nodes and 1716 elements (Figure 7). All of the elements were linear quadrilaterals.

MODEL INPUT

For steady-state groundwater flow simulations, ATLAS-SOLUTE requires input of parameters that characterize the transmissive properties of the UFS, as well as those that permit quantification of contributions to and losses from the UFS. Numerical input components used in the model are as follows:

- Water-table configuration
- Base of the UFS and saturated thickness
- Aquifer hydraulic conductivity

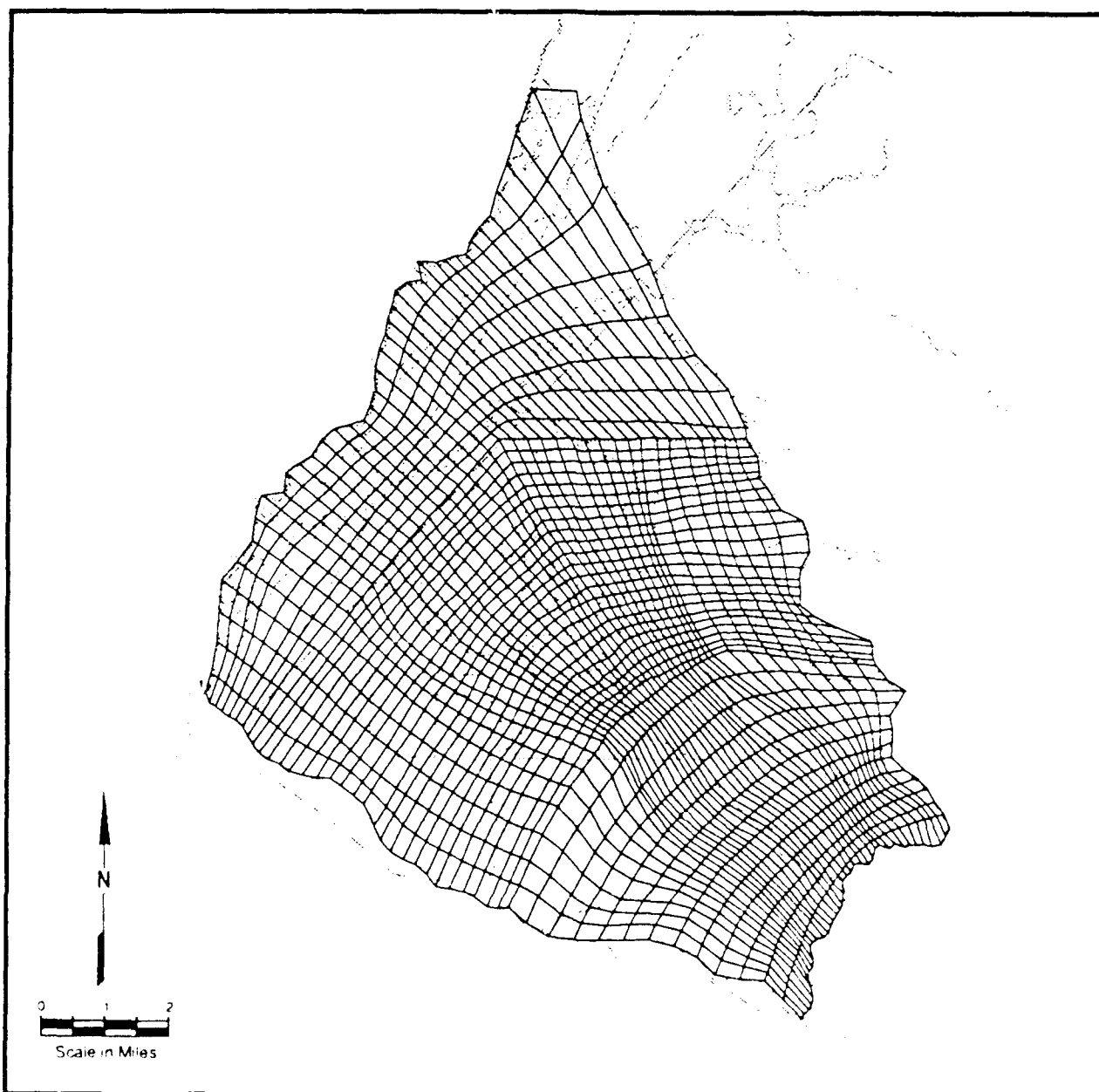


Figure 7: Finite Element Mesh

- Stream and lake seepage properties
- Irrigation recharge estimates
- Other recharge
- Inflow from the Denver Fm
- Groundwater withdrawals
- Boundary underflows

Each of these components is discussed separately below.

Water-Table Configuration

The regional model is based on a steady-state water-table configuration that uses hydraulic head data collected primarily from 1981 through 1987. Most of these data were collected from monitoring wells located within RMA boundaries. The water-table map shown in Figure 8 illustrates the most significant features of shallow groundwater movement in the study area.

The prevailing flow direction from southeast to northwest is apparent. Also shown is a groundwater mound that occurs near the center of the model in the vicinity of the South Plants. The presumed cause of this feature is recharge in an area where the UFS exhibits low hydraulic conductivity (May, 1982). However, the source of this recharge (e.g., precipitation, leaky sewer pipes) is not certain.

Figure 8 also indicates areas where considerable inflow to the UFS occurs as boundary underflow. The most obvious of these areas is the southeast model boundary formed by the Highline Canal. Another underflow source area occurs along the lower reaches of Second

Creek in the northernmost part of the study area. Underflow is also observed, although more subtly, along a portion of Sand Creek immediately southwest of the southwestern corner of RMA.

Base of Unconfined Flow System and Saturated Thickness

A contour map of bedrock (i.e., the alluvium-Denver Fm contact) elevations in the study area was prepared. The bedrock map was in turn overlain with the previously described water-table map (1981 through 1987 mean levels) to delineate areas of unsaturated alluvium. It is in these areas that the modeled UFS is assumed to consist of the upper Denver Fm, as shown in Figure 9.

In areas of saturated alluvium, the base of the unconfined aquifer has been assumed to equal bedrock elevation. However, the conceptual model also requires that the base of the UFS be defined in areas where the alluvium is unsaturated (i.e.,

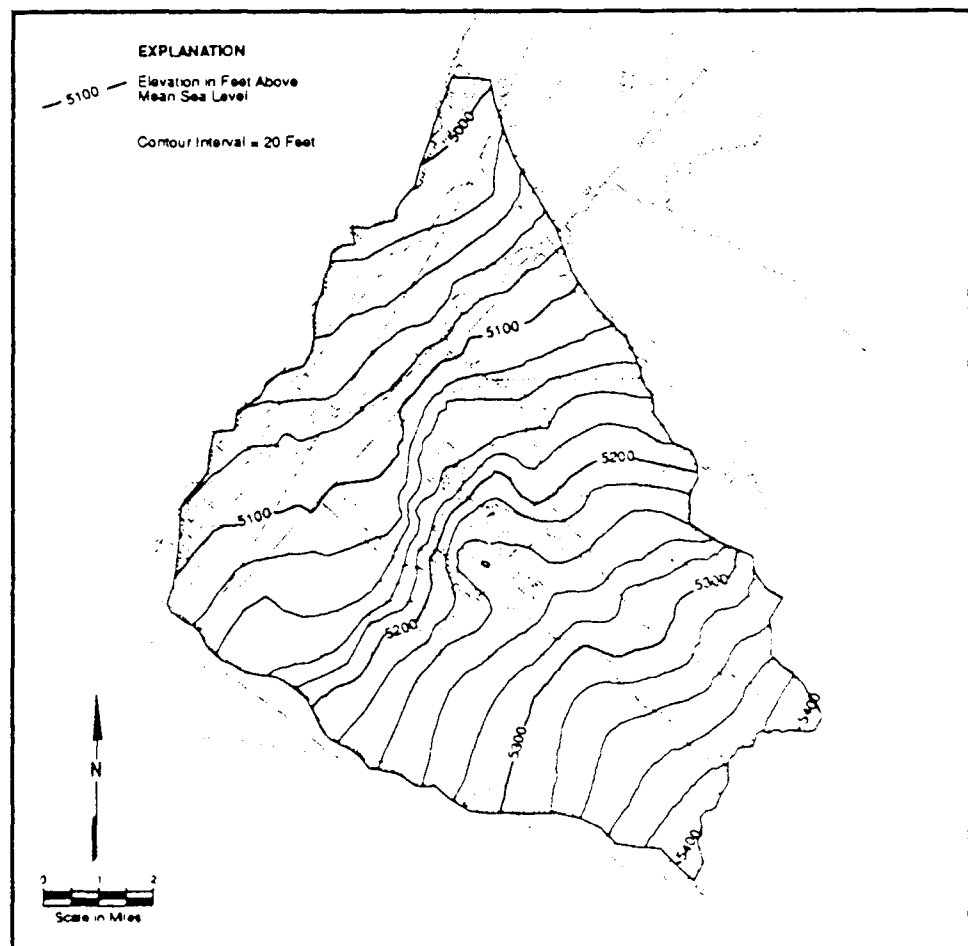


Figure 8: 1981 - 1987 Mean Water Table

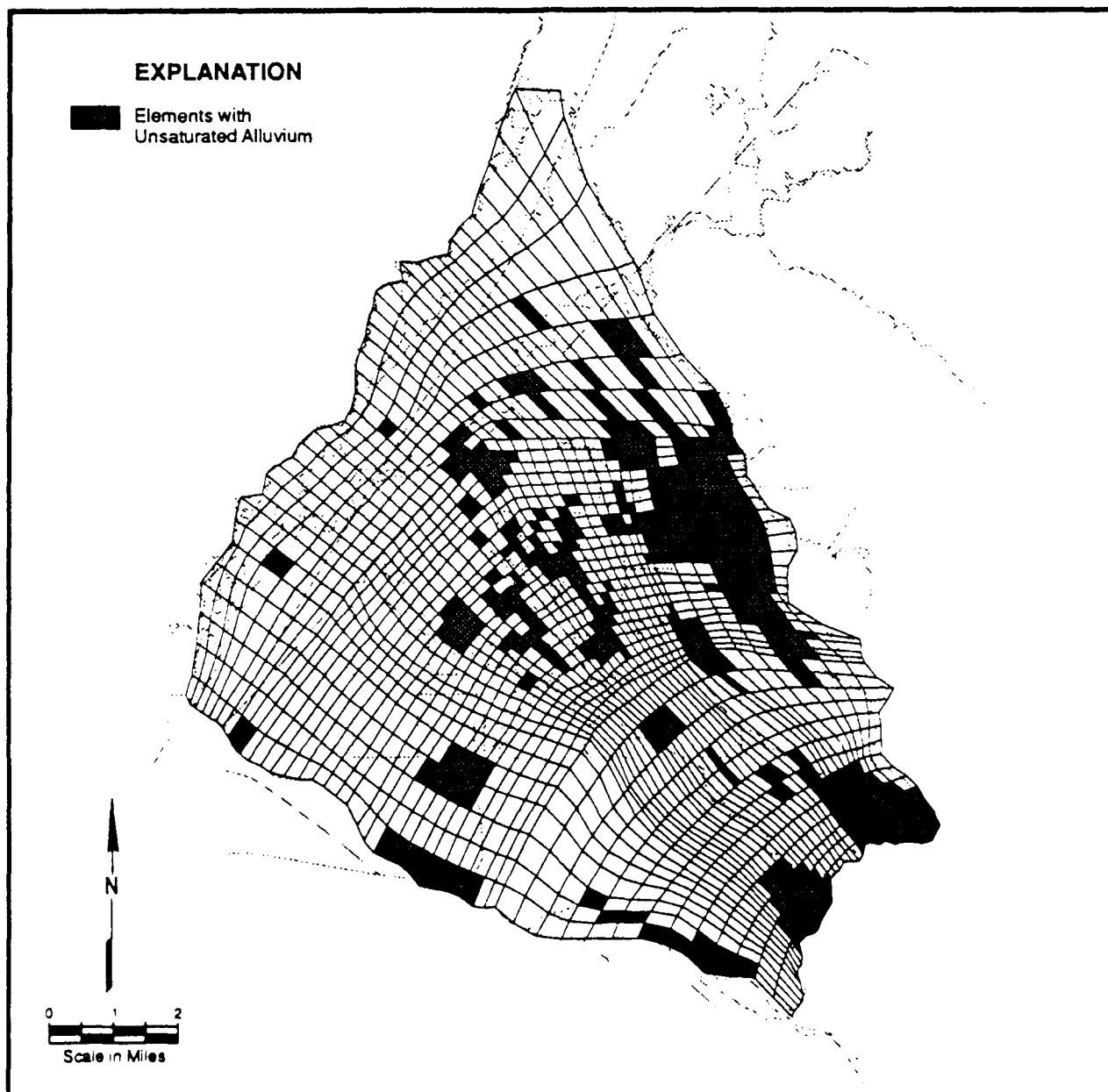


Figure 9: Elements with Unsaturated Alluvium

where the upper Denver Fm comprises the flow system). Because no distinct stratigraphic unit exists in the Denver Fm to define the base of the UFS in these areas, the base of the UFS was initially estimated by linear interpolation between bedrock elevations on either side of each isolated section of upper Denver Fm. The schematic of Figure 5 helps show how this was accomplished. A straight line connecting the bedrock surface on either side of the Denver Fm island in Figure 5 was used to define initial values for the base of unconfined aquifer elevations within it.

The above procedure was followed to produce a contour map delineating base-of-aquifer elevations. The corresponding map depicting saturated thickness of the unconfined aquifer (water-table elevation minus base of the UFS) is presented in Figure 10. Paleochannels in the study area, which coincide with zones of greater saturated thickness, are discernible in the saturated thickness map. As Figure 10 indicates, aquifer saturated thickness in some paleochannels exceeds 60 feet.



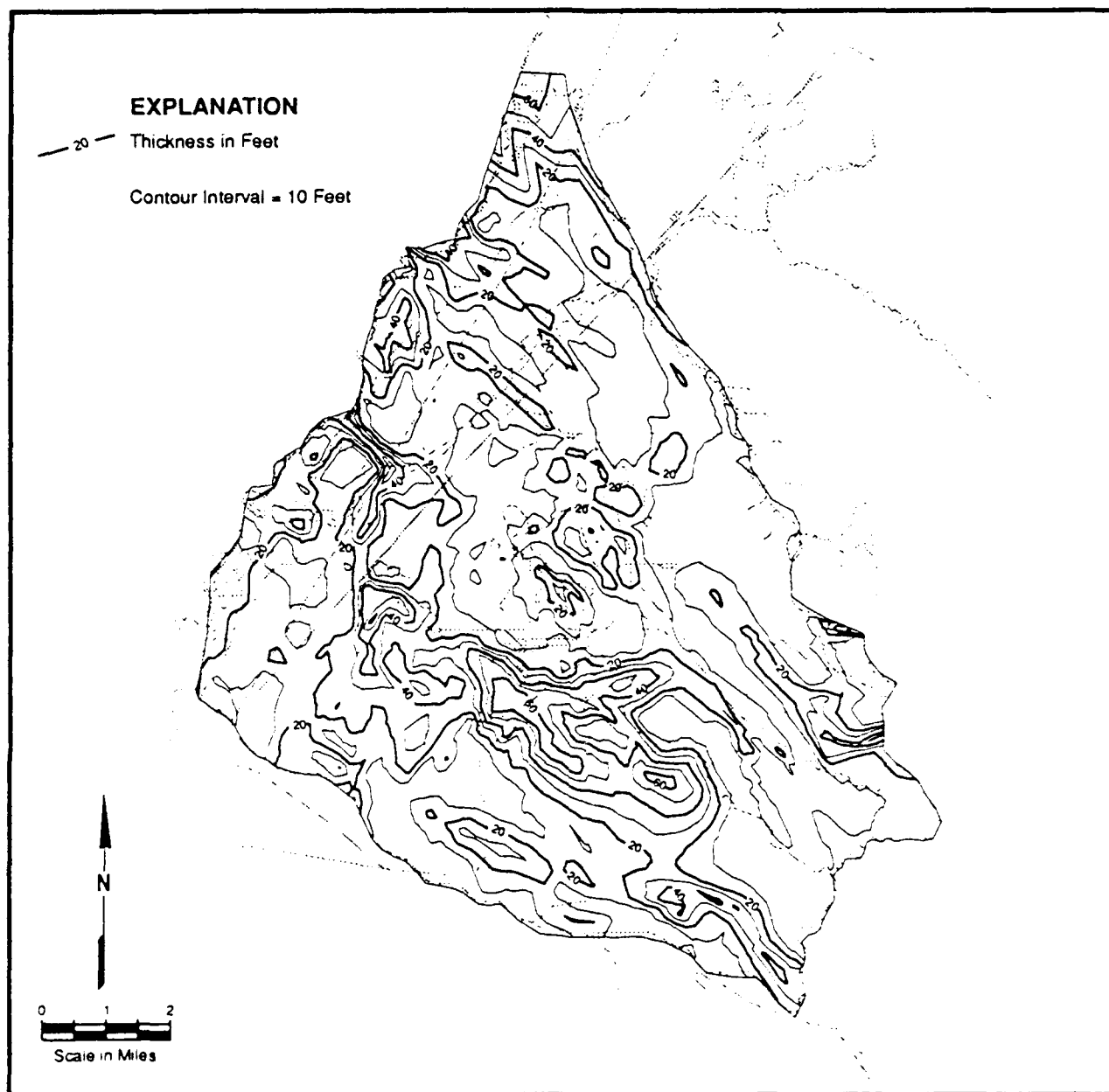


Figure 10: Saturated Thickness of the Unconfined Flow System

Aquifer Hydraulic Conductivity

Hydraulic conductivities were assigned to each of the 1716 elements comprising the regional model. Initial estimates of hydraulic conductivity were based on boring logs, aquifer test analyses, and geologic interpretations of depositional environment. Seven different material classes were initially used, each characterized by a representative hydraulic conductivity and a possible range of hydraulic conductivity values. The largest hydraulic conductivities were assigned to those areas associated with South Platte River terrace

deposits and the paleochannels that transect them; the smallest hydraulic conductivities were assigned to Denver Fm elements (i.e., elements of unsaturated alluvium in Figure 9). Eolian deposits of relatively low hydraulic conductivity dominate the interfluvial zones situated between paleochannels in upgradient parts of the model. Values of representative hydraulic conductivity ranged from 0.3 ft per day (ft/day) to 850 ft/day. During calibration of the regional model, attempts were made to maintain this initial distribution of material types and to keep hydraulic conductivity



ties within the range designated for each material. Although this was not possible in all instances, the general initial conductivity distribution was largely adhered to.

Stream and Lake Seepage Properties

Exchange of water between surface waterways and the UFS was simulated in the regional model using a head-dependent stream seepage algorithm. The algorithm permitted a stream or canal to lose water to the UFS in areas where the stream surface exceeds water-table elevation. Discharge of groundwater to the stream or canal occurred in areas where the water table exceeds stream surface elevation. Furthermore, the streambed was assumed to consist of a thin, semi-permeable clogging layer. Under cases of disconnection, in which a distinct unsaturated zone separated the clogging layer from the underlying water table, the rate of seepage loss from the stream was assumed to be constant and independent of water-table elevation.

ATLAS-SOLUTE required input values for streambed elevation, stream surface elevation, clogging layer hydraulic conductivity and thickness, and streambed area. Because detailed information on the elevation profiles of many streams and canals does not exist, streambed elevations were often estimated from U.S. Geological Survey (USGS) 1:24000 topographic maps. When a streambed elevation was established, the next step was to determine a reasonable value for stream depth from which stream surface elevation could also be derived. For some streams and canals, this latter parameter could be determined using stream flow and rating curve information provided by others. Alternatively, some stream depths were derived by assuming uniform flow in the waterways and then calculating (with Manning's Equation) the depth on the basis of observed average flows, stream width, and reasonable estimates of stream slope. When no data existed that permitted such determinations, flow depth was arbitrarily assumed to equal 1 ft. Estimates of stream width were also required for many waterways.

Previous determinations of stream loss (e.g., MKE, 1987) were used to derive reasonable values for the clogging layer properties of many of the streams and canals. Streambed conductance (the ratio of the clogging layer hydraulic conductivity to the clogging layer thickness) was

calculated on the basis of the average stream loss rate, streambed elevation, local water-table elevation, and assigned values of stream depth and stream width. When this was not possible, the stream conductance was estimated.

Initially, attempts were made to develop representative values of stream seepage parameters for individual reaches of streams for which spatially variable data were available. However, subsequent model calibration runs indicated that this approach only marginally altered simulated heads. Consequently, uniform average values were in most cases assigned to the entire unlined portion of each waterway. Exceptions were made to this latter approach for the Burlington Canal and First Creek.

The parameters controlling lake seepage were handled in the same manner as stream seepage. As in the case of stream seepage, lakebed conductances resulted from data analysis and minor changes of this parameter during model calibration.

Irrigation Recharge Estimates

As previously discussed, the rate of irrigation recharge applied in the regional model is equal to the recharge rate developed by Konikow (1977) and assumed by MKE (1987) for irrigated parts of the RMA region. This rate, 1.9 ft per year (ft/yr), is based on the assumption that approximately 45 percent of an applied irrigation rate of 4.2 ft/yr ends up in the saturated zone of the UFS. The elements to which irrigation recharge has been assigned are located primarily between the South Platte River and the Burlington Canal. Irrigation recharge also occurs in a few isolated zones south of RMA.

Other Recharge

Recharge rates in residential and commercial/industrial areas were applied in the regional model at rates varying between 2.3 inches per year (in./yr) and 3.6 in./yr. Estimates of volumetric recharge from Basins A through F lying north of the South Plants region were developed using a variety of sources. The recharge quantities from Basins A, B, C, and E were from MKE's (1987) regional recharge estimates. Basin D recharge was assumed to be the average of the MKE (1987) estimate for this component from 1975

through 1981 and observations made in 1986 and 1987 (Ebasco and others, 1989) indicating that Basin D was dry. The value for Basin F recharge adopted in the regional model (0.004 cubic ft per second [cfs]) is from Miller (1979). Recharge quantities from residential, commercial/industrial, and basin sources were treated as specified inflows in the regional model.

Care was taken in the regional model not to superimpose the assumed areal recharge from precipitation in undeveloped and unirrigated areas on the recharge already assigned under the previous categories. To accomplish this, the assumed areal recharge rate of 0.25 in./yr (MKE, 1987) was applied only to elements in which recharge from other sources was not applied. The total recharge applied to the model representing areal recharge from precipitation was 1.02 cfs (458 gallons per minute [gpm]).

The volumetric recharge rate assigned to the South Plants area in the regional model was 0.045 cfs (20 gpm). This value was half of that used in the Konikow (1977) model for this component. In the regional model, the South Plants recharge was divided equally among eight elements and was added to the 1.02 cfs already included in the model as recharge from precipitation.

Inflow from the Denver Formation

Estimated inflows to the UFS from updip flow within the Denver Fm were developed in the regional model using hydraulic conductivities of 0.3 ft/day in areas where the aquifer HGUs within the Denver Fm were believed to subcrop (Ebasco and others, 1989; MKE, 1989); a hydraulic conductivity of 0.03 ft/day was used elsewhere. The assumed hydraulic gradient in all calculations for recharge caused by updip flow in the Denver Fm was 0.008 ft/ft, which is typical of measured gradients within Denver Fm units (Ebasco and others, 1989). To compute unit thicknesses, it was assumed the Denver Fm beds intercept the base of the UFS at an average angle of 4 degrees. The resulting computed inflow to the UFS within the model area from all Denver Fm sources was 0.427 cfs.

Groundwater Withdrawals

Irrigation pumping was handled by withdrawing 0.02 cfs from each of the 103 irrigation wells. A

total of 5.49 cfs of groundwater was withdrawn from the nine South Adams County Water and Sanitation District wells. Groundwater withdrawal and injection rates associated with the North Boundary Containment System (NBCS) were approximately 0.52 cfs. The equivalent pumping/injection rate for the Northwest Boundary Containment System (NWBCS) was 0.41 cfs. Pumping and injection rates at the Irondale Boundary System (IBS) totaled 2.68 cfs.

Boundary Underflows

Initial estimates of groundwater underflow across the boundaries formed by the Highline Canal, Sand Creek, and Second Creek were determined by simple Darcy's Law calculations. The calculations were made using initial estimates of hydraulic conductivity values, hydraulic gradients developed from the observed water-table configuration of Figure 8, and saturated thicknesses shown in Figure 10. The magnitudes and spatial distribution of these boundary inflows were varied during the steady-state calibration until a reasonable match with observed water-table elevations was achieved.

MODEL CALIBRATION

A trial-and-error, ad-hoc procedure was employed to calibrate the steady-state regional flow model. The model calibration procedures are described in this section.

The parameters adjusted the most during calibration were hydraulic conductivity and saturated thickness. To a lesser extent, some adjustments were made to prescribed inflows (underflow) across the boundaries formed by Highline Canal, Sand Creek, and Second Creek. Streambed and lakebed elevations and stream and lake depths were kept at constant values during the calibration procedure. Streambed conductances were allowed to change only minimally.

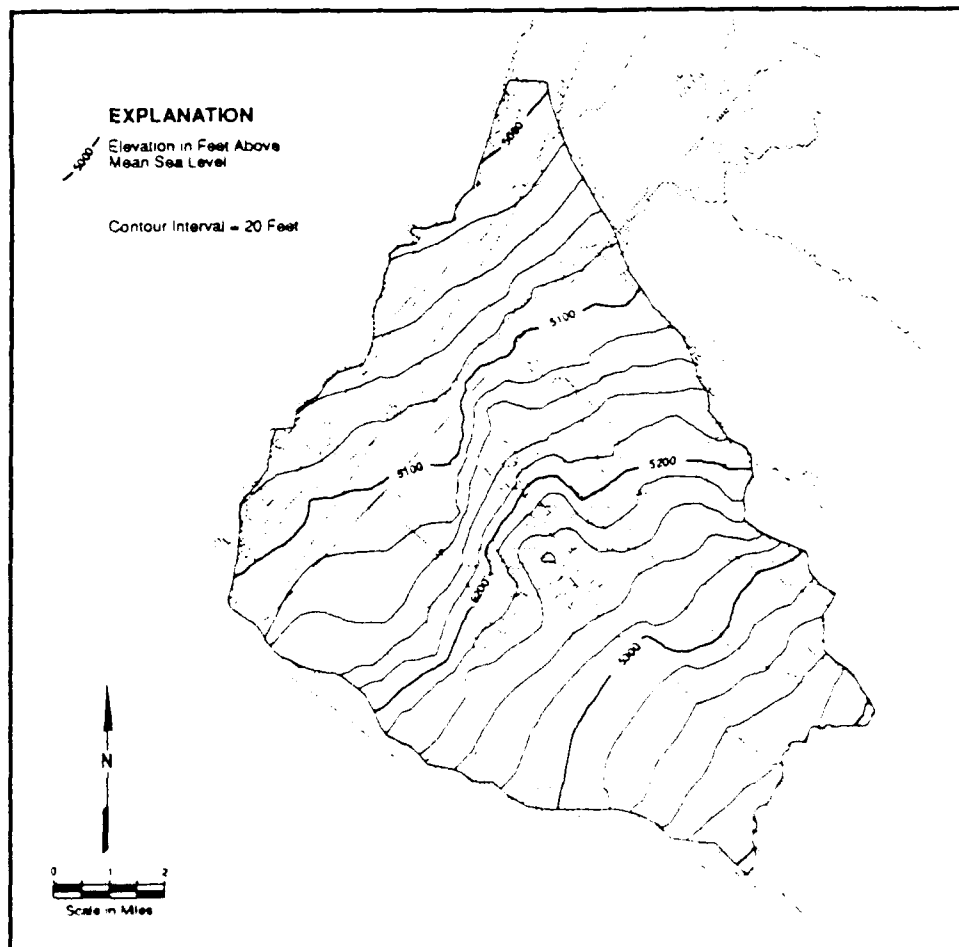
More than 100 calibration runs were made. Such a large number of runs was needed because the model exhibited a very strong sensitivity to the low hydraulic conductivities assigned to elements representing the Denver Fm and adjacent areas. After completion of each run, a contour map of differences between observed and computed heads was prepared to locate areas where differences remained relatively large. This map was

often overlaid on maps showing the most recent hydraulic conductivity and saturated thickness distributions to help facilitate adjustments to these parameters for the next run. Groundwater flows at selected points within the model domain were also periodically checked to ensure that model-computed flows were similar to those that were measured or estimated from field data (such as at the boundary containment systems). The model was assumed to be calibrated when it appeared that further runs did little to improve the matching of observed heads or measured flows.

A contour map of computed hydraulic heads from the last calibration run (Figure 11) shows the calibrated numerical model does a reasonable job of duplicating the general southeast-to-northwest flow pattern and the groundwater mound in the South Plants area.

Analysis of the differences between observed and computed heads for the calibrated model showed

that the differences were not concentrated in any single area. Within the RMA boundary (onpost), the largest differences occurred in the vicinity of unsaturated alluvium where the model simulates flow in the upper Denver Fm. This observation was attributed partly to the high sensitivity of the model to the low hydraulic conductivities assigned to the upper Denver Fm and nearby areas, and partly to the uncertainty of observed water levels and other hydrogeologic parameters descriptive of these areas. Relatively large differences between observed and computed water levels were also observed in offpost areas south and southeast of RMA. The model is considered uncertain in these latter areas because the data are extremely sparse. A cumulative distribution of absolute values of differences between observed heads and computed heads indicated that the overall model fit was relatively good for the regional scale; more than 85 percent of the 1800 nodes in the model exhibited absolute head differences of 8 ft or less.



Eleven different groups of hydraulic conductivity were used to provide the best fit achieved by the calibrated regional flow model. The seven initial hydraulic conductivity values were augmented primarily by adding values at the low end of the range of hydraulic conductivity. These additional values were mostly used for achieving calibration in areas where groundwater flow is relatively low, and near areas of unsaturated alluvium, the South Plants area, Basins A through F, and in interfluvial zones. Hydraulic conductivities in the calibrated model ranged from 0.5 ft/day to 2000 ft/day.

Figure 11: Computed Water-Table Elevations

MODEL RESULTS

The calibrated regional model was used to:

- Illustrated flow paths in and around RMA
- Analyze hydrogeologic budget for the study area
- Summarize gains and losses for streams and lakes within the study area
- Quantify groundwater flow rates in the UFS at locations in and around RMA

The following sections present the results of the above analyses.

Flow Paths

Several flowlines indicating regional groundwater flow paths have been generated with the calibrated model. Because the model is steady state, the flow lines are equivalent to streamlines.

Streamlines in the regional model have been delineated using a particle tracking algorithm included in an

ATLAS-SOLUTE postprocessor. This technique moves particles through the domain by using computed Darcy's Law velocity vectors determined for each node. The resulting flowlines for 12 separate particles are shown in Figure 12. The point of release for each particle has been selected such that the flowlines generally follow major routes of groundwater flow. This means that most particles eventually tend to be entrained in the flow paths associated with paleochannels. A cursory comparison of the flowlines presented in Figure 12 with mapped contaminant plumes in the region (Ebasco and others, 1989) indicates the regional model does

a reasonable job of predicting flow paths in areas north of the RMA north boundary and north and northwest of the RMA northwest boundary.

Water Budget

The steady-state hydrologic budget produced by the model for the study area is summarized in Table 1, which shows the relative importance of various inflow and outflow components affecting the regional flow domain. Pertinent findings regarding the model budget are as follows:

1. The largest sources of water are seepage losses from surface waterways and lakes in the study area. The combined contribution to the UFS from these components accounts for over 48 percent of all water sources.
2. The next largest contributors to the regional system are irrigation recharge and boundary inflows (underflow). The combined contribution from these two sources, along with losses

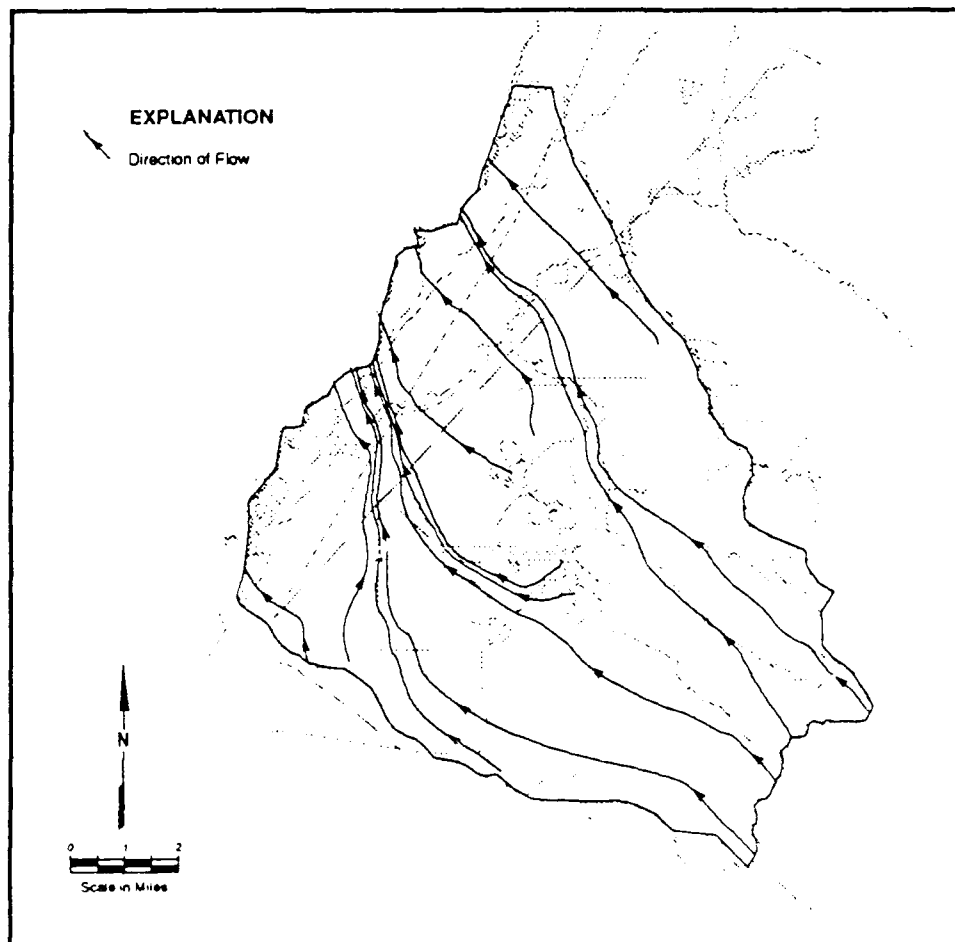


Figure 12: Flowlines in the Regional Model

INFLOW		
Source	Flow (cubic feet per second)	Percent of Total
Boundary inflow (underflow)	9.107	15.70
Irrigation	9.043	15.59
Stream and canal seepage	25.883	44.63
Lake and pond seepage	2.351	4.05
Basins	0.072	0.12
South Plants recharge	0.045	0.07
Recharge in developed area	1.936	3.34
Recharge from precipitation	1.021	1.76
Gravel pits	4.562	7.87
Denver Formation	0.427	0.74
North Boundary Containment System	0.470	0.81
Northwest Boundary Containment System	0.407	.70
Irondale Boundary System	2.672	4.61
Total	57.996	99.99
OUTFLOW		
Discharge		
South Platte River	37.985	65.46
Other streams	0.578	1.00
Gravel pits	7.167	12.35
Lake and pond seepage	1.310	2.26
Irrigation wells	2.060	3.55
South Adams County Water and Sanitation District wells	5.487	9.45
North Boundary Containment System	0.470	0.81
Northwest Boundary Containment System	0.407	0.70
Irondale Boundary System	2.566	4.42
Total	58.030	100.00

Table 1: Steady-State Hydrologic Budget

from the surface-water bodies, accounts for more than 80 percent of all the inflow. Thus, the recharge attributed to Denver Fm updip flow and infiltration of precipitation, including that portion that collects as ponded runoff in basins and depressions, has a minor influence on the total flow system.

- Most groundwater leaves the unconfined aquifer by seepage to the South Platte River (approximately 65 percent of total discharge) and the gravel pits lying immediately south of the South Platte River (approximately 12 percent of total).
- The next largest discharge mechanisms are losses to surface-water bodies, other than the

South Platte River and nearby gravel pits, and pumping (South Adams County Water and Sanitation District). The combined discharges to all surface-water bodies, plus pumping, account for all groundwater leaving the system. Thus, the calibrated model indicates that no other discharge processes affect regional flow. This may be somewhat misleading because the model budget of Table 1 does not reflect system outflow caused by consumptive use by crops and other vegetation. The model implicitly takes consumptive use processes into account in irrigation recharge and other recharge estimates.



Streams and Lakes

Model-computed gains and losses for most of the streams and lakes in the study area are listed in Table 2. These quantities show that the greatest losses and, therefore, the greatest contributions to the UFS occur along the Burlington Ditch, O'Brian Canal, and the Fulton Ditch, which are immediately south of and approximately parallel to the South Platte River. Such high losses are attributed to the fact that these waterways tend to carry large flows, are largely disconnected from the underlying water table, and are underlain by relatively permeable alluvium. Second Creek appears to be both a losing and gaining stream, with most of the gains in Second Creek occurring along its upper reaches within the modeled area. According to the model, Sand Creek is primarily losing water to the UFS.

Table 2 shows the model computes a loss of 0.101 cfs for the onpost portion of First Creek. This compares relatively well with an estimated 0.20 cfs of net loss determined by MKE (1987) using field data for this reach of First Creek. It is difficult to adjust the regional model so that computed losses on First Creek closely match mea-

sured losses. Much of the onpost portion of First Creek is apparently connected to the UFS by saturated media; consequently, slight variations in computed head in the numerical model can easily cause computed seepage values (and the direction of seepage between stream and aquifer) to differ considerably from observed behavior on First Creek.

The revised regional model computes a loss of 0.004 cfs for First Creek between the northern boundary of RMA and O'Brian Canal. It is unclear if First Creek generally behaves as a gaining or losing stream along this offpost reach. MKE (1987) treated First Creek north of the RMA north boundary as site for net groundwater discharge. Ebasco and others (1989) indicated that this reach of First Creek gains and loses water, depending on locations, season, and streamflow conditions. Monitoring of First Creek during 1986 and 1987 showed that net losses occurred from the stream north of the RMA north boundary.

Model-determined gains and losses for lakes on RMA that appear to remain connected to the UFS are also quite sensitive to computed water-table elevations. The regional model shows a combined

Surface-Water Body	Loss (cubic feet per second)	Gain (cubic feet per second)	Net (cubic feet per second)	
First Creek				
Onpost	0.101	0.00	0.101	Loss
North of Rocky Mountain Arsenal				
North Boundary	0.004	0.00	0.004	Loss
All of First Creek	0.126	0.187	0.06	Gain
Uvalda Interceptor	0.398	0.00	0.398	Loss
Highline Lateral	0.770	0.035	0.735	Loss
Fulton Ditch	4.563	0.00	4.563	Loss
Burlington Ditch	13.154	0.00	13.154	Loss
O'Brian Canal	4.742	0.00	4.742	Loss
Highline Canal	0.199	0.029	0.170	Loss
South Platte River	1.424	37.985	36.561	Gain
Sand Creek	0.081	0.001	0.080	Loss
Second Creek	0.191	0.258	0.067	Gain
Bull Seep Ditch	0.122	0.060	0.062	Loss
Ladora Lake	0.483	0.860	0.377	Gain
Lake Mary	0.00	0.094	0.094	Gain
Upper Derby Lake	0.026	0.304	0.278	Gain
Lower Derby Lake	0.922	0.052	0.870	Loss
Havana Pond	0.920	0.00	0.920	Loss
Rod and Gun Club	0.067	0.00	0.067	Loss
Sand Creek Lateral	0.046	0.008	0.038	Loss

Table 2: Computed Gain and Loss Rates for Streams and Lakes



Flow Quantities at Selected Sites

It is likely the flow system north of Basin F has

The combined flow to the RMA north boundary (Figure 13) determined by the revised regional model is 0.51 cfs. This value is very close to a measured average rate of groundwater withdrawal of 0.52 cfs from all discharge wells at the NBCS (Figure 13) during fiscal years 1984, 1986, and 1987 (Car, 1987).

The calibrated model computes a total net discharge to the South Platte River of 36.2 cfs.

For the 11.94 miles of river simulated in the model, this represents a river gain of 3.03 cfs per mile. This value is slightly higher than a computed gain of 2.95 cfs per mile determined from results presented in Konikow's (1977) model.

SUMMARY AND CONCLUSIONS

A numerical model of regional groundwater flow at RMA has been constructed. The model simulates steady-state, two-dimensional areal flow in an UFS that comprises shallow alluvium and upper Denver Fm materials where the alluvium is unsaturated. Calibration of the model is primarily based on mean water-table elevations for the period 1981 through 1987.

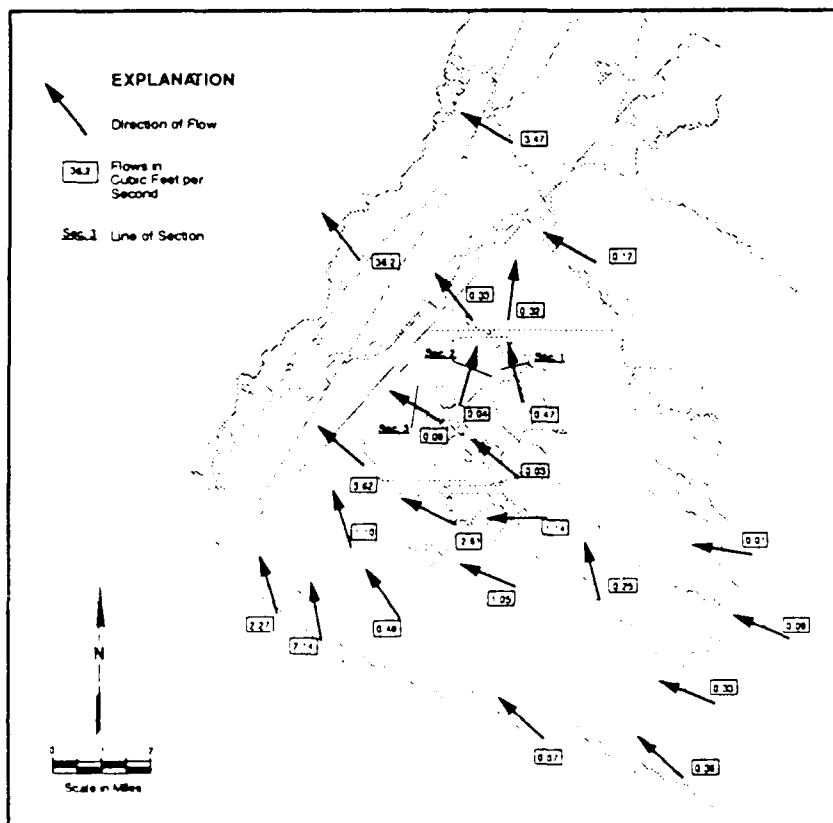


Figure 13: Volumetric Flows at Selected Sites

The regional model is part of what was intended to be an organized set of models for assessing groundwater quality remedial actions at RMA. It was anticipated that the area encompassed by the regional model would be divided into subregions for which more detailed contaminant transport models could be prepared. Computed results from the regional model could be incorporated into the local, subregional models in the form of boundary conditions or calibrated hydraulic parameters.

By simulating flow in the upper Denver Fm in areas where the alluvium is unsaturated, the regional model attempts to account for groundwater movement across zones that are frequently treated as impermeable in other models of flow and transport (Konikow, 1977). However, this approach to simulating shallow groundwater movement cannot be verified because of the large uncertainties in upper Denver Fm hydraulic parameters. Partly because of the inherent uncertainties associated with flow simulation in the Denver Fm, results of the regional model, particularly within or near areas of unsaturated alluvium, should be considered approximate.

Conclusions from this regional groundwater flow modeling study are as follows:

1. Inclusion of the upper Denver Fm as part of the UFS in areas where the alluvium is unsaturated provides one possible mechanism for explaining groundwater flow across areas that have previously been treated as impermeable and therefore incapable of transporting contaminants.
2. The overall effect that Denver Fm contributions to the UFS have on regional groundwater flow is probably minimal. Flows from the Denver Fm probably exert the greatest influence in areas of relatively low groundwater flow, such as in the South Plants area and near Basins A through F.
3. The largest sources of recharge to the UFS appear to be infiltration losses from Burlington Ditch, O'Brian Canal, and the Fulton Ditch, all of which are located immediately south of the South Platte River. Large losses from these waterways are attributed to the fact that these waterways carry large flows, are underlain by coarse alluvial sediments, and have a tendency to remain disconnected from the UFS.
4. Most groundwater outflow from the region occurs as discharge to the South Platte River. The regional model shows a net gain of 36.2 cfs for the 11.94 miles of the river that border the study area, which translates into a gain of 3.03 cfs per mile.
5. The calibrated regional flow model indicates that relatively large underflows occur across model boundaries on the lower reaches of the Sand Creek and Second Creek and across the southeastern model boundary formed by the Highline Canal.
6. Development of the regional groundwater flow conceptual model and calibration of the numerical model have helped delineate areas of large parameter uncertainty. The areas of greatest uncertainty in the study area are mostly south and east of RMA, where few wells exist and hydrogeologic data are limited. Considerable uncertainty also exists for areas within RMA boundaries, including areas of low flow near South Plants and Basins A through F. Parameters affecting flow in Denver Fm materials are also highly uncertain. Insufficient data exist to accurately distinguish areas where updip flow in Denver Fm aquifers discharges to the UFS from zones where the UFS loses water through leakage across aquitards.



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Treatment of Metal-containing Soil and Sludge by the Ceramic Bonding Process

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ABSTRACT

New results are presented on the treatment of a zinc-contaminated pond soil, a groundwater remediation sludge containing cobalt, chromium, nickel and zinc, and an electroplating filter cake waste containing zinc. These wastes were acquired from the Riverbank Army Ammunition Plant at Riverbank, California.

The CBI technology involves thermally-driven, chemical bonding of metal-bearing wastes into the silicate structure of ceramics. The most remarkable feature of the CBI process is that the metals are rendered insoluble, not only in weak acid leaching tests (e.g. TCLP, or California WET), but also in hot, concentrated nitric and hydrochloric acids (California's TTLC). Because the samples are pulverized to minus 50-mesh (40-400 μm) before analysis, the process represents a chemical synthesis, and not a simple encapsulation.

The CBI process and equipment (patents pending) are described, and results from bench and prototype experiments are presented. Three principal conclusions are drawn from the experiments. First, the acid solubility of metals bonded in the CBI ceramic aggregate was very low, typically a few percent of California's TTLC and STLC limits. Second, presence of the metal in the ceramic product was confirmed by hydrofluoric acid digestion, indicating that the reduction in solubility of metals was due to bonding, rather than vaporization or other loss. And third, bench and prototype experiments agreed well, demonstrating that the CBI process is effective in a continuously operating device.

Ceramic Bonding, Inc. (CBI) was founded in 1987 to develop technology for reliable, inexpensive, *on-site* conversion of heavy metal hazardous wastes to safe, useful materials, such as construction aggregates. CBI's principal mission is to provide equipment that can be used by industry to eliminate the need for costly and environmentally unwise disposal of toxics at Class I dumpsites. The effectiveness of this new technology for use in remediation activities as well as metal plating process sludges is described in this paper.



BACKGROUND

In 1987, the reported generation of hazardous heavy metal wastes in California was 140,000 ton/yr.¹ The U.S. Congressional Budget Office estimated national hazardous metal waste production to be 55 million tons in 1983.² Through April, 1989, the U.S. Environmental Protection Agency (EPA) had identified over 900 acutely dangerous hazardous waste disposal sites that required immediate cleanup through the Superfund program, and another 27,000 sites that may potentially qualify.³ Ultimately, the U.S. General Accounting Office believes that up to 425,000 waste sites will require cleanup in the next 50 years, at a cost of up to \$100 billion.³

Enterprises which generate hazardous heavy metal wastes are facing escalating costs and increasing restrictions on the transportation, storage, and physical properties of their wastes. Disposal charges, currently \$300-1000 per ton, are expected to increase, especially in California, where a prohibition on the dumping of untreated hazardous wastes at Class I dumpsites is being phased in.⁴ Waste producers are limited to 90 day on-site storage of toxics⁵, and disposers of hazardous wastes also face potentially costly, long-term legal liability.

Ceramic Bonding, Inc. has developed a unique (patented) process and specialized equipment (patent pending) to render metal-bearing wastes harmless. The technology involves high temperature, physical-chemical bonding of metals into naturally occurring aluminosilicates, to produce a non-soluble, non-leachable ceramic aggregate. Results from solubility and leaching tests on the CBI ceramic product (Armorite™) have been presented previously.^{6,7} These prior data have dealt with first-generation wastes such as filter cake from the treatment of electroplating waste water, waste glass frit from a ceramic processing facility, and waste casting sand from a brass foundry. Prior to the current work, no data were available on the effectiveness of the CBI process with contaminated soils or sludges from groundwater cleanup.

This paper describes the CBI process and some of the associated chemistry. New results are presented on the treatment of a zinc-contaminated pond soil, a groundwater remediation sludge containing cobalt, chromium, nickel and zinc, and an electroplating filter cake waste containing zinc. These wastes were acquired from the Riverbank Army Ammunition Plant at Riverbank, California. Strong and weak acid solubility characteristics of the bonded ceramic material are presented.

PROCESS

The CBI process⁸ is an endothermic, physical-chemical bonding of metal ions into aluminosilicate crystals in a high temperature environment. The process is accomplished in two stages: proportioning and mixing of the ceramic additive material with the metal waste; and thermal processing.

Proportioning and mixing is accomplished in the CBI system by commercially available feeders and blenders. Once mixed, the material is pelletized to a size and shape which is mechanically and thermally appropriate for further processing. The mixing and pelletizing are performed continuously, and are monitored by a supervisory control system. Adequate bonding will occur for a wide range of waste/additive

stoichiometries, however it is economically desirable to maintain mixture ratios and moisture contents within pre-determined limits.

In the CBI thermal process, the pellets are first dried and then heated to the required chemical bonding temperature. Upon reaching the necessary temperature, the metal ions combine chemically with the aluminosilicate additive. The metal ions diffuse into the void regions between tetrahedrally shaped aluminosilicate molecules. Concurrently, the chemically bonded water molecules, which were incorporated in the original aluminosilicate crystals, are removed, and a type of sintering takes place. After sintering, the material is cooled and discharged. Appropriate residence times for each of the above processes are assured by careful design of the thermal processor, and through the automatic control system, which monitors and governs the material throughput rate and temperature profile.

EXPERIMENTAL RESULTS

Metal Extraction and Leaching Tests.

Waste Sources. Samples of industrial metal-bearing wastes have been processed in our laboratory under various conditions to evaluate the CBI technology. At this writing, samples from twenty-two different waste streams, waste blends and reagent-grade chemicals have been tested, some of which were reported previously.^{6,7} The waste samples evaluated for this study are identified as A through D. Their constituent hazardous elements are presented in Table 1. The samples were acquired in small quantities from the Riverbank Army Ammunition Plant at Riverbank, California.

Table 1 - Metal Waste Sources

- A. Contaminated Soil from Evaporation Ponds - containing zinc.
- B. Hydroxide Precipitate Filter Cake from Electroplating Rinsewater - containing zinc.
- C. Sludge Precipitated from Groundwater Remediation - containing cobalt, chromium, nickel and zinc.
- D. Combination of Wastes A, B and C above.

Metal Sources. List of waste samples, their constituent metal elements, and the type of industrial process the waste was derived from.

Waste sample A contained moderate concentrations of zinc from prior wastewater evaporation activities. It was received as a coarse material and was screened to remove rocks and then pulverized before testing with the CBI process. The pond soil moisture content was approximately 8%, as received.

Waste samples B and C were hydroxide precipitate sludges prepared from two sources of contaminated water. Waste B is a filter cake generated as a by-product of normal treatment of electroplating wastewater from the plant. Waste C was generated by precipitating metal hydroxides from a sample of contaminated groundwater undergoing remediation. The moisture content of each of the sludge samples was consistent, at approximately 33%, as received.

Waste D was a combination of the A, B and C, in dry-weight proportions of 81%, 18% and 1%, respectively.

Analyses. The standard California tests⁹ for solubility in strong and weak acids were performed on three types of samples (waste, unfired, and fired) for a total of 12 samples tested. Analytical testing was performed by a state-certified laboratory, and results were compared to California TTLC (strong acid) and STLC (weak acid) limits¹⁰. Where not otherwise identified, percentages are by weight.

A chemical analysis of the CBI ceramic additive, a naturally-occurring aluminosilicate material, is given in Table 2. The material was received as approximately 80 percent minus-325 mesh (44 μ m).

Table 2 - CBI Ceramic Additive

Al ₂ O ₃	29-30	%	SiO ₂	51-55	%
Fe ₂ O ₃	2-5	%	CaO	0.1-0.3	%
MgO	0.5-0.8	%	Na ₂ O	0.2-0.7	%
KO	1.5-2.0	%	L.O.I.	10-14	%

Ceramic Additive. Chemical analysis of the aluminosilicate additive used for experiments described here. The Loss-on-Ignition (L.O.I.) is primarily water (H₂O), bound chemically to the silicate matrix. Percentages are by weight.

Strong Acid Solubility. The HNO₃ solubility of metals will be described first. Table 3 presents concentrations of acid-soluble metals in three types of samples: (1) waste, (2) unfired waste/additive mixture, (3) fired ceramic/metal product (Armorite™). Sample types (1) and (2) were dried and all samples were pulverized to minus-50 mesh (297 μ m) prior to analysis. The ratio of additive to waste (dry mass basis) is shown in the table. The product samples were fired in an electric laboratory furnace at approximately 2000 °F for 30 minutes.

The results of Table 3 show several important features of the CBI process as applied to these metal-bearing wastes. The most significant feature of the CBI process has been described previously^{6,7} and is reconfirmed with these data: The concentrated, hot, nitric acid (Calif. TTLC, or EPA #3050) extraction procedure dissolves only a fraction of the metals present in the Armorite™. In order to break silicate bonds and quantify the metals present in the Armorite™, a standard digestion procedure using hydrofluoric acid was performed. In the cases here, only 9 to 17 percent of the metals digested by the HF procedure were soluble in HNO₃. Again, it should be highlighted that the samples were pulverized to minus-50 mesh before analysis, ruling out macro-encapsulation as the means whereby the metals were rendered insoluble.

Table 3 - Solubility Results

	<u>RATIO</u>	<u>1. WASTE</u>	<u>2. UNFIRED</u>		<u>3. FIRED</u>	
	<u>Add/Waste</u>	<u>HNO₃-Extract</u>	<u>HNO₃-Extract</u>	<u>HF-Digest</u>	<u>HNO₃-Extract</u>	<u>HF-Digest</u>
	<u>kg/kg</u>	<u>mg/kg</u>	<u>mg/kg</u>	<u>mg/kg</u>	<u>mg/kg</u>	<u>mg/kg</u>
A. Pond Soil						
Zinc	2/1	4970	1660	1540	186	1550
B. Electroplating Filter Cake						
Zinc	7/1	36300	4890	4560	526	4130
C. Groundwater Sludge						
Chromium	4/1	2680	468	570	111	647
Cobalt	4/1	18800	2870	3140	403	3860
Nickel	4/1	143	42	71	14	95
Zinc	4/1	2300	842	903	89	956
D. Combination of A, B, and C						
Zinc	2.9/1	10974	3060	2500	170	1950

Solubility Results. Soluble metal concentrations as determined by HNO₃/HCl extraction (EPA Procedure 3050, or California's TTLC test). HF digestion was conducted similar to the EPA 3050 procedure, except that HF was substituted for HCl. Digestion of silicate compounds by HF allows measurement of total metal concentration in fired and unfired samples. All samples were dried and pulverized to minus-50 mesh before conducting leaching or extraction procedures. The waste sources (A-D) are identified in Table 1.

Digestion with HF. The difference in HF-digestion concentration between "waste" and "unfired" samples is due to dilution by the ceramic additive. Some uncertainty exists in the apparent dilution factor ("Waste" concentration/"Unfired" concentration) for two reasons. First, the analytic procedure has some inherent uncertainty associated with both the wet chemical extraction and the subsequent spectrographic analysis. Since the procedures were conducted by an outside laboratory, no estimate of the analytical uncertainty is given here. Second, the additive itself contains trace amounts of these metals in different concentrations, and this will influence the soluble concentration of the unfired material, especially for those wastes initially low in the concentration of a given metal. Approximate trace metal concentrations in the ceramic additive are presented in Table 4.

The HF procedure is used to verify that metal concentration effectively remains constant as a result of firing, however, variation also exists in the comparison of HF digestion results from "unfired" and "fired" samples. A number of factors may have contributed to this variation. First, during each HF digestion procedure, a solid residue was observed to remain undissolved. Since the spectrographic analysis was performed on the solution, not the residue, complete quantification of the metals is not guaranteed. Second, the change in HF-Digestion concentration between "unfired" and "fired" (after accounting for L.O.I. from bound water) was not consistent among the waste types, some increasing and some decreasing. Consequently, no broad



conclusions can be made with regard to metal retention upon firing. A more narrow conclusion can be asserted, however: the decrease in HNO₃ solubility of metals after firing is due to bonding, and not vaporization or other loss.

This conclusion is especially significant for an element such as cadmium, whose vapor pressure is high at the CBI processing temperatures, and might be at risk for loss if the chemical bonding did not occur quickly relative to vaporization. In our prior work⁸, cadmium was seen to be effectively retained, as measured by HF digestion. Recent research¹¹ has shown that "preheater" rotary cement kilns are 99 percent effective in trapping and "recycling" volatile metals such as cadmium. Because the tests described here and previously⁸ were conducted in a benchtop laboratory furnace, they represent the worst case scenario of zero internal recycling of volatiles. The continuous Ceramicbond™ equipment is inherently more effective than a rotary kiln (or a laboratory furnace) at accomplishing the sort of recycling described¹¹.

Table 4 - Trace Metal Concentrations in Ceramic Additive

<u>Element</u>	<u>Concentration (mg/kg)</u>
Cadmium	<0.5
Chromium	92.6
Copper	59.8
Lead	<5.0
Nickel	56.2
Zinc	59.7

Trace Metal Concentrations in Ceramic Additive. Approximate metal concentrations as determined by HF Digestion in a sample of the CBI aluminosilicate (ceramic) additive. The sample was dried and screened to verify 100 percent passing 50 mesh before conducting the digestion procedure.

Leaching Results. Table 5 shows TTLC, STLC and TCLP concentrations of metals from the Armorite™ product, as compared to regulatory limits. For each metal in every waste, the Armorite™ solubility was more than a factor of 9 lower than the regulatory limits. Results from EP Toxicity tests conducted previously⁷ on different materials were comparable to TCLP results cited here.

Product Attributes and Physical Characterization.

Physical Tests. Physical characterization of the Armorite™ ceramic aggregate was not performed as part of the current study, however our prior studies^{6,7} have shown the Armorite™ material to possess high strength and low density, when compared to a standard concrete aggregate such as Ottawa Sand, which is used in A.S.T.M. testing procedures for strength of Portland Cement mortar.

Scanning Electron Microscope photographs were taken of unfired and fired samples of the Pond Waste material. In the unfired sample, discrete particles of waste and reagent were seen, whereas in the fired sample, a homogeneous, fused mass is present. It was inferred from the Micrographs that the waste had diffused into the aluminosilicate reagent and was inaccessible to leaching.

Table 5 - Leaching Results

	LIMIT			ARMORITE™		
	<u>TTLC</u> mg/kg	<u>STLC</u> mg/liter	<u>TCLP</u> mg/liter	<u>TTLC</u> mg/kg	<u>STLC</u> mg/liter	<u>TCLP</u> mg/liter
A. Pond Soil						
Zinc	5000	250	---	186	1.8	---
B. Electroplating Filter Cake						
Zinc	5000	250	---	526	9.2	---
C. Groundwater Sludge						
Chromium	2500	560	5	111	0.42	0.032
Cobalt	8000	80	---	403	2.1	0.441
Nickel	1000	5	---	14	0.45	0.184
Zinc	5000	250	---	89	2.3	0.587
D. Combination of A, B, C						
Zinc	5000	250	---	170	2.5	---

Leaching Results. Leachable metal concentrations as determined by California's TTLC and STLC tests, and compared to regulatory limits. The STLC procedure is similar to the federal EP Toxicity, and the TTLC is identical to the federal EPA #3050 procedure. All samples were dried and pulverized to minus-50 mesh before conducting leaching or extraction procedures. The waste sources (A-D) are identified in Table 1.

Commercial Uses. Preliminary tests indicate the Armorite™ aggregate is suitable for blending into a manufactured ceramic product. One example where the Armorite™ might be used commercially is the manufacture of ceramic tiles and bricks. In this process, a small fraction of pre-fired material is sometimes added to the unfired raw materials for improved product integrity. This pre-fired material, or grog, is normally acquired by brick makers from their own output, typically in the form of defective or broken product, but often as reground, saleable, finished bricks and tiles. By using Armorite™ as grog instead of reground product, ceramic material manufacturers may experience higher yields and lower unit costs. Based on tests with a small amount of Armorite™, a local ceramic producer has judged the material to be a very desirable substitute for reground-product grog. Another potential use for Armorite™ would be as a coarse or fine aggregate in asphaltine or portland cement concrete. Tests are planned to compare the Armorite™ properties to the aggregate specifications issued by the California Department of Transportation.

Equipment Performance.

The performance of the CBI process with Waste A was evaluated in our prototype thermal processor, which produces approximately 1 ton/day of Armorite™ product. The results were very favorable. On 1 August, 1990 an eight-hour test was run demonstrating that appropriate temperatures and residence times could be achieved with the Riverbank material. The fired ceramic material was very hard, similar to the material fired in the laboratory furnace. Its color was somewhat darker than material containing only the aluminosilicate reagent, without pond soil.

The fired sample was analyzed by TTLC, STLC and HF Digestion. These results are presented in Table 6. The zinc was very effectively bonded in the continuous CBI thermal processor. The TTLC and STLC solubilities were comparable to those of samples fired in the laboratory furnace.

Table 6 - Bonding of Zinc in Continuous Thermal Processor

	<u>STLC</u> mg/liter	<u>TTLC</u> mg/kg	<u>HF Dig.</u> mg/kg
<i>Fired in Laboratory Furnace</i>	1.8	186	1550
<i>Fired in Continuous Thermal Processor</i>	3.8	198	1910

Bonding in Continuous Thermal Processor. Soluble metal concentrations as determined by STLC, TTLC and HF Digestion tests. All samples were dried and pulverized to minus-50 mesh before conducting extraction procedures. The source of zinc was from the Pond Soil (Waste A, Table 1).

CONCLUSION

Ceramic Bonding, Inc. has developed new technology for reliable, inexpensive, and on-site conversion of hazardous, heavy-metal industrial wastes to safe, useful, construction materials. The CBI process has been described, with some discussion of the thermally-driven, metal/aluminosilicate bonding chemistry.

These results were our first opportunity to describe the efficacy of the Ceramic Bonding process with contaminated soils and groundwater remediation sludges. Results from solubility and leaching tests have been presented demonstrating the large reduction in metal solubilities achieved by CBI thermal processing. The Armorite™ ceramic material was shown to pass California's STLC and TTLC hazardous waste regulatory limits with large safety margins.

Physical-chemical and mechanical properties of the bonded CBI aggregate have been examined, verifying the macroscopic and microscopic stability of the material and its suitability for use in manufactured ceramic products. Tests in our proprietary thermal processor have shown that the CBI process can work very effectively in a continuously operating device.

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TECHNICAL AND ECONOMIC EVALUATION
OF
AIR STRIPPING FOR VOLATILE ORGANIC COMPOUND (VOC) REMOVAL
FROM
CONTAMINATED GROUNDWATER
AT
SELECTED ARMY SITES

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ABSTRACT

This report provides a process and economic evaluation of the use of air stripping to remove VOCs from contaminated groundwater on or near three existing U.S. Army facilities. The three sites visited were:

- Twin Cities Army Ammunition Plant (TCAAP), Minneapolis, Minnesota
- Letterkenny Army Depot (LEAD), Chambersburg, Pennsylvania
- Sharpe Army Depot (SHAD), Lathrop, California

The evaluation focused on the economics of each site to determine (1) the total capital cost for the existing treatment facilities, (2) the operating costs for each existing facility, and (3) the significant cost drives for each facility.

The three sites varied in design and operating philosophy due to the geographical locations and the demands placed on the systems. TCAAP and LEAD required heavy freeze protection while SHAD required none. LEAD included carbon absorbers while TCAAP and SHAD had none. Materials of construction varied from steel to fiberglass-reinforced plastic (FRP) to plastics (PVC).

The installed costs of each facility were determined and compared using total life cycle costing (TLCC) analysis based on 1,000 gallons of water treated over the life of each plant. The operating costs were also determined and compared based on 1,000 gallons of water treated.

The work was conducted by a project team from the Development Division of Tennessee Valley Authority's National Fertilizer & Environmental Research Center (NFERC) under Army Contract No. TV-79415T. The study was conducted for the United States Army Toxic and Hazardous Materials Agency (USATHAMA) under a scope of work originally proposed in July 1989.



INTRODUCTION

This report provides a process and economic evaluation of the use of air stripping to remove VOCs from contaminated groundwater on or near Army facilities. The main objective of the study was to determine the capital and operating costs for existing Army facilities. Additionally, the practices of VOC stripping are described in detail.

Data for the study were obtained from three existing air-stripping facilities at (1) Twin Cities Army Ammunition Plant (TCAAP) near Minneapolis, Minnesota; (2) Letterkenny Army Depot (LEAD) in Chambersburg, Pennsylvania; and (3) Sharpe Army Depot (SHAD) in Lathrop, California. An investigation was performed at each site to (1) determine the capital costs for the existing treatment facilities, (2) determine the operating costs for the existing facilities, and (3) identify significant cost factors for each of the facilities.

Because of the different locations and demands placed on the stripper units, the three facilities vary in design and operating philosophy. The size of the units range from 200 gallons/minute at LEAD to 2,900 gallons/minute at TCAAP. The TCAAP and LEAD units are located in cold climates and require extra freeze protection, while the unit at SHAD is essentially in the open. The unit at LEAD also contains liquid- and vapor-phase carbon absorbers to further reduce the VOC emissions; this was found to be a major cost item from both a capital and an operating standpoint.

The operating personnel requirements vary according to the level of sophistication of the control and data-gathering equipment installed at each unit.

The materials of construction of the strippers and piping systems varied widely and include steel, fiberglass-reinforced plastic (RFP), and plastics (PVC).

The existing units were found to be operating within the required environmental discharge limits.

BACKGROUND (PROCESS DESIGN)

Principles of Air Stripping

Air stripping represents controlled contact of a liquid containing volatile contaminants with a clean stream of air. Ideally, the entire volatile component is transferred from the liquid to the air/vapor phase. In a liquid-vapor contactor, such as a packed-column air stripper, the mass transfer rate from liquid to vapor is controlled by approaches to the equilibrium concentration of the compounds in the water and the air at the specified conditions. This mass transfer capability is represented by Henry's Law constant of each compound in the liquid and gaseous phases.

Henry's Law constant reflects the relative volatility of each compound; that is, how easily the compound can be transferred from the liquid to the vapor.



According to Henry's Law, the concentration of VOC in the water and the air will be a function of the total VOC vapor pressure. Values for Henry's Law constants for various compounds can be either calculated or obtained from literature. Compounds with large Henry's Law constants are more easily removed from the water stream than compounds with lower values. Henry's Law constants are very temperature dependent. Many VOCs can be air stripped at ambient temperature; however, those compounds with low volatilities at ambient temperature may require preheating of the groundwater before it enters the stripper.

Air stripping offers effective VOC removal at reasonable capital and operating costs. Air stripping is probably the most common method used in removing VOCs from groundwater, especially where the groundwater contamination involves low solvent concentrations (in the $\mu\text{g/L}$ range) and in areas of the country where the treatment facility is located in remote locations. Under these conditions, air stripping is favored since VOC-laden exhaust air can often be released uncontrolled to the atmosphere without significant impact on ambient air quality. When effluent water quality is critical, multiple air strippers (in series) can often be used to remove VOCs below detectable limits.

Carbon absorption can also be used in conjunction with air stripping to remove VOCs from the groundwater; however, this method is much more expensive than air stripping alone. Carbon absorption, although highly effective, is not normally used unless the influent water quality is such that air stripping by itself will not purify the water.

The efficiency of air strippers is dependent not only upon the Henry's Law constant of the VOCs in the water stream, but also on the packing in the tower, the air flow rate and temperature, and the liquid flow rate and temperature. The amount of packing used in the tower will be determined based on the diameter and height of the tower. The type of packing is also of importance.

For most air strippers, the diameter of the tower will depend upon the quantity of air and water being handled, physical and chemical properties of the water, and the ratio of air to water. The height of the tower, as well as the total packing volume, depends on the influent concentration of the groundwater and the desired effluent concentration of the water, as well as the mass transfer/unit of the packing. Most tower shells are constructed of the least expensive and the most durable material available. Fiberglass-reinforced plastic is most common, although carbon steel or other alloys may be used.

Column Packing

Packing in an air stripper is designed to increase the liquid surface area exposed and to allow even distribution of liquid and vapor over the cross section of the tower. Characteristics of packing are an important consideration in column design; the packing will contribute greatly to the overall performance of the stripper.

The packing should be able to operate over a wide range of gas-to-liquid (G/L) ratios and be resistant to entrainment, corrosion, fouling, and fracturing.



Column packing comes in a myriad of materials, forms, and sizes; and is of three basic types: (1) random dump, (2) structured grid, and (3) high-efficiency mesh. Random-dump packing normally ranges from 0.5 to 3.5 inches in diameter. It may be of various configurations, for example, ring-shaped or saddle.

Liquid Distributors

In order for packing to perform properly, the liquid must be distributed evenly over the packing surface area. Often, poor column performance is a result of improper or inadequate liquid distributors. A wide variety of distributors are available, each having advantages and disadvantages. A V-notched distributor has a high potential turndown, low fouling potential, and high maximum flow rate. The water is distributed by troughs with V-shaped notches along the sides. V-notched distributors are suitable for columns that are greater than or equal to three feet in diameter. These distributors operate by gravity flow and are level sensitive. Columns containing V-notched distributors must be level for optimum operation performance. To avoid leveling problems from fixed distributors, liquid distribution can be accomplished using spray nozzles. However, spray nozzles are subject to fouling, have low turndown ratios, limited maximum flow rates, and high pressure drop in the nozzles.

Design Criteria for Air Strippers

Factors affecting design of air strippers are the water flow rate, water temperature, contaminant concentration, and allowable effluent limits. Other factors which will play a role in the design and operation of the air stripper include being able to ensure proper cleanliness of the tower, the structural integrity of the tower, the tower packing, and the internals as well as distributors and support plates.

Tower Packing

Wall effect is greater with small-diameter towers. Tower columns should have internal features to redistribute drippage and support packing. A good rule of thumb is to use packing material in size which is 1/10 the diameter of the column itself. If the ratio of tower diameter to packing diameter is less than 8:1, the liquid tends to flow out of the packing and down the walls of the column. This is known as channeling.

SITE DESCRIPTIONS

Twin Cities Army Ammunition Plant (TCAAP)

TCAAP is located in New Brighton, Minnesota, about 13 miles north of Minneapolis/St. Paul in northwestern Ramsey County. It covers approximately four square miles. The installation was constructed in 1941 and 1942, and was used for the production, inspection, and storage of ammunition until 1957. After a period of standby the site was used again from 1966 through 1974.

Previous studies have shown that underground water aquifers at TCAAP are contaminated with a variety of VOCs. These contaminants and concentrations are:



<u>Influent</u>	<u>Concentration, $\mu\text{g/L}$</u>
1,1-dichloroethylene	160
1,1-dichloroethane	47
cis-1,2-dichloroethylene	56
Chloroform	3
1,1,1-trichloroethane	950
Trichloroethylene	3,400
Tetrachloroethylene	3

It has also been determined that most of these VOCs in the groundwater can be traced to the methods of disposal of explosives, solvents, oil, and other organic materials at TCAAP. In an attempt to properly remediate the underground aquifer at TCAAP, it was decided that the most cost-effective method would be to build a water treatment site which employed the use of VOC packed-tower strippers using ambient air as the cleaning medium. Figure 1 is a photograph of the water treatment site at TCAAP. Figure 2 is a flowsheet of the process as it is currently being operated. The water treatment site at TCAAP consists of four air strippers which are operated on a continuous basis to process approximately 2,900 gallons/minute (gal/min) of water. The treatment unit originally consisted of three towers, but the fourth tower was added in 1988 when pumping capacity to the plant was increased to 2,900 gal/min. The towers (numbered 1 to 4) are enclosed in a heated metal building to a height of 8 feet; the remaining portion of the towers extend through the roof of the enclosure. Each tower has a total height of 34 feet. The effective packing height of each tower is 24.5 feet. The towers are constructed of carbon steel. The piping associated with the towers is ductile iron. Towers 1 and 2 are both 7 feet in diameter, while towers 3 and 4 are 8 feet in diameter. The four towers serve to make up two trains which operate in parallel. Tower 1 and 4 operate in series to form train 1, while tower 2 and 3 are operated in series to form the second train. A 16-inch-diameter inlet water line to the treatment plant carries about 2,900 gal/min to the plant. Once the water supply enters the enclosure, it splits and the lines reduce to 8 inches in diameter and carry 1,450 gal/min of water each to towers 1 and 2. After the water exits the outlet of tower 1, it enters a wet well. From this wet well, the water is pumped up to the top of tower 4 for its final scrubbing.

The water pumped into the top of tower 2 exits into a second wet well. From here, the water is pumped to the top of tower 3 for final scrubbing of VOCs. The clean water from towers 3 and 4 is mixed as it exits each tower and enters a third wet well. All three wet wells are 20 feet by 20 feet by 8 feet in size. The water from the third wet well is pumped through a 16-inch-diameter line to a gravel and sand pit where the water is allowed to reenter the underground water table. The gravel and sand pit is located on site, about 5,300 feet from the water treatment facility. The same deposit at the gravel pit represents an ideal discharge point for allowing the water to filter back into the underground aquifer.

Towers 1, 2, and 3 all use three-inch Intalox saddles for packing, while tower 4 uses three-inch lanpac. Each tower has its own separate blower. Air is blown countercurrent to the flow of water in each tower. The blower capacity for towers 1 and 2 is 5,100 cubic feet/minute (ft^3/min) of air. The blower capacity for towers 3 and 4 is 9,850 ft^3/min . For towers 1 and 2, the air: H_2O mass ratio is 26:1; while for towers 3 and 4, the air: H_2O ratio is 50:1.



Figure 1
VOC Water Treatment Plant at Twin Cities Army Ammunition Plant

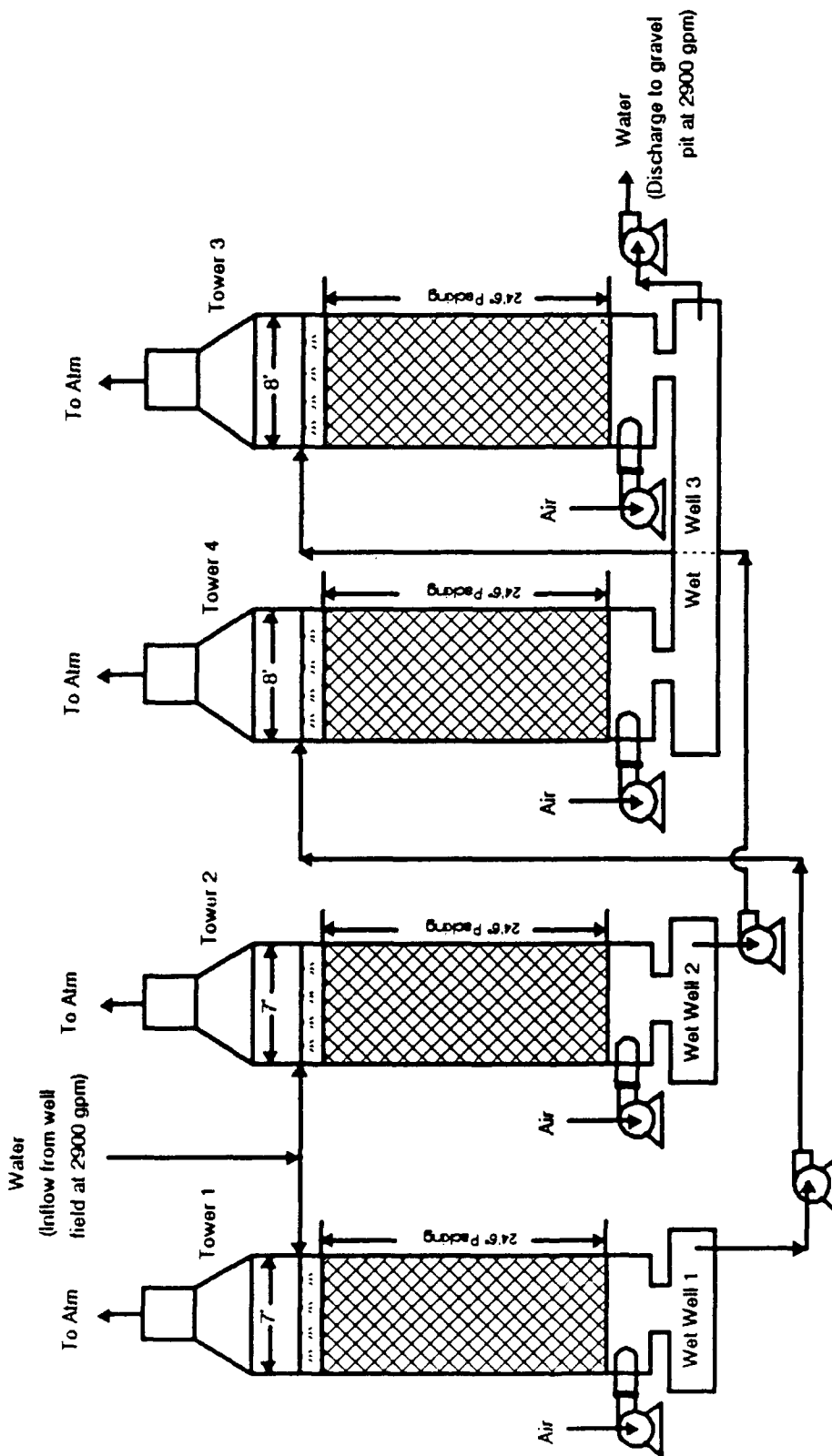


Figure 2
Flowsheet of Water Treatment Plant at Twin Cities Army Ammunition Plant

The contaminated water is pumped to the treatment site from 12 boundary wells and 4 source control wells which are located in areas identified as having underground contaminated water. Each well has its own separate pump which is totally enclosed for cold weather protection. The typical pumphouse is constructed of 8-inch concrete blocks and is about 8 feet by 13 feet in size. The four source control wells pump either 45 or 60 gal/min of water. All of the well pumps have a 6-inch impeller except for one boundary well pump which has a 4-inch impeller. The discharge on each pump is constructed of schedule 40 galvanized steel with a recovery well steel casing enclosing each pump. Each pump has a turbo flow meter located inline to monitor the water rate. There is also a motorized check valve and gate valve located at each pump.

The forcemain collection system includes a pumphouse for each of the 16 pumps along with 16 return well structures and associated valves and controls. The return pipe is installed in a trench 7 feet underground and ranges in size from 6 to 16 inches in diameter. The piping in the forcemain is constructed of ductile iron.

The plant is equipped to operate automatically with little need for constant staffing of personnel. An operator normally makes routine visits to the plant once each day. The operator will spend approximately one hour at the site checking the system, recording meter readings, and making minor repairs.

Letterkenny Army Depot (LEAD)

LEAD is located in Franklin County, Pennsylvania, about 5 miles north of the city of Chambersburg, Pennsylvania. The depot was established in 1942 with the primary mission of ammunition storage and shipping. Since 1942, the depot's mission increased to include (1) overhauling, rebuilding, and testing of wheeled and tracked vehicles; (2) issue and shipment of chemicals and petroleum products; and (3) maintenance, demilitarization, and modification of ammunition. Operations currently conducted at the depot include cleaning and stripping, plating, lubrication, demolition, chemical and fuel oil transfer, and storage and washout/deactivation of ammunition. Several of these activities involve the use of trichloroethylene, other solvents, lubricants, corrosives, and various metals. LEAD is the owner/operator of two industrial wastewater treatment plant (IWTP) lagoons. Initially, there was only one lagoon which was built between 1954 and 1957. It was unlined and had an operating capacity of one million gallons. This unlined lagoon reportedly contained sludges, oils, and industrial wastes. The sludge and waste material leaked from the bottom of the lagoon into the underground water aquifer resulting in contamination of the groundwater.

In 1967, the lagoon was rebuilt to prevent further leakage. There are now two concrete-reinforced lagoons constructed within the original lagoon perimeter. The current concrete-lined lagoons remain potential contaminant sources due to cracks discovered in the bottom of the southern lagoon. The active use of these lagoons has been totally discontinued since December 1987 in preparation for their closing.

Two significant volatile compounds historically identified in groundwater near the IWTP lagoons are trichloroethylene and trans-1,2-dichloroethylene. The listing of VOCs found in the groundwater along with the concentration of each contaminant is given as the following:



<u>Influent</u>	<u>Concentration, µg/L</u>
1,1,1-trichloroethane	666
1,1-dichloroethylene	810
trans-1,2-dichloroethylene	700,000
Trichloroethylene	370,000
Tetrachloroethylene	34

In order to remediate the groundwater at the IWTP lagoons, a water treatment plant was built which utilized air stripping followed by carbon adsorption. Filtration pretreatment was added to the facility based on reports of water quality, which were received from the initial well drilling and testing of the groundwater. These tests indicated the presence of 80 to 160 micrograms/liter (µg/L) of suspended solids in the samples. Initial treatment provided a system of wells capable of continuously pumping 80 gal/min of contaminated groundwater from near the IWTP lagoons to remove the VOCs. Air stripping was selected as the primary treatment technology. However, because of concerns from the Pennsylvania Department of Environmental Resources (PADER), a carbon absorption system was also incorporated into the air-stripping facility so that the exit air and exit water would be treated with carbon before being discharged from the plant.

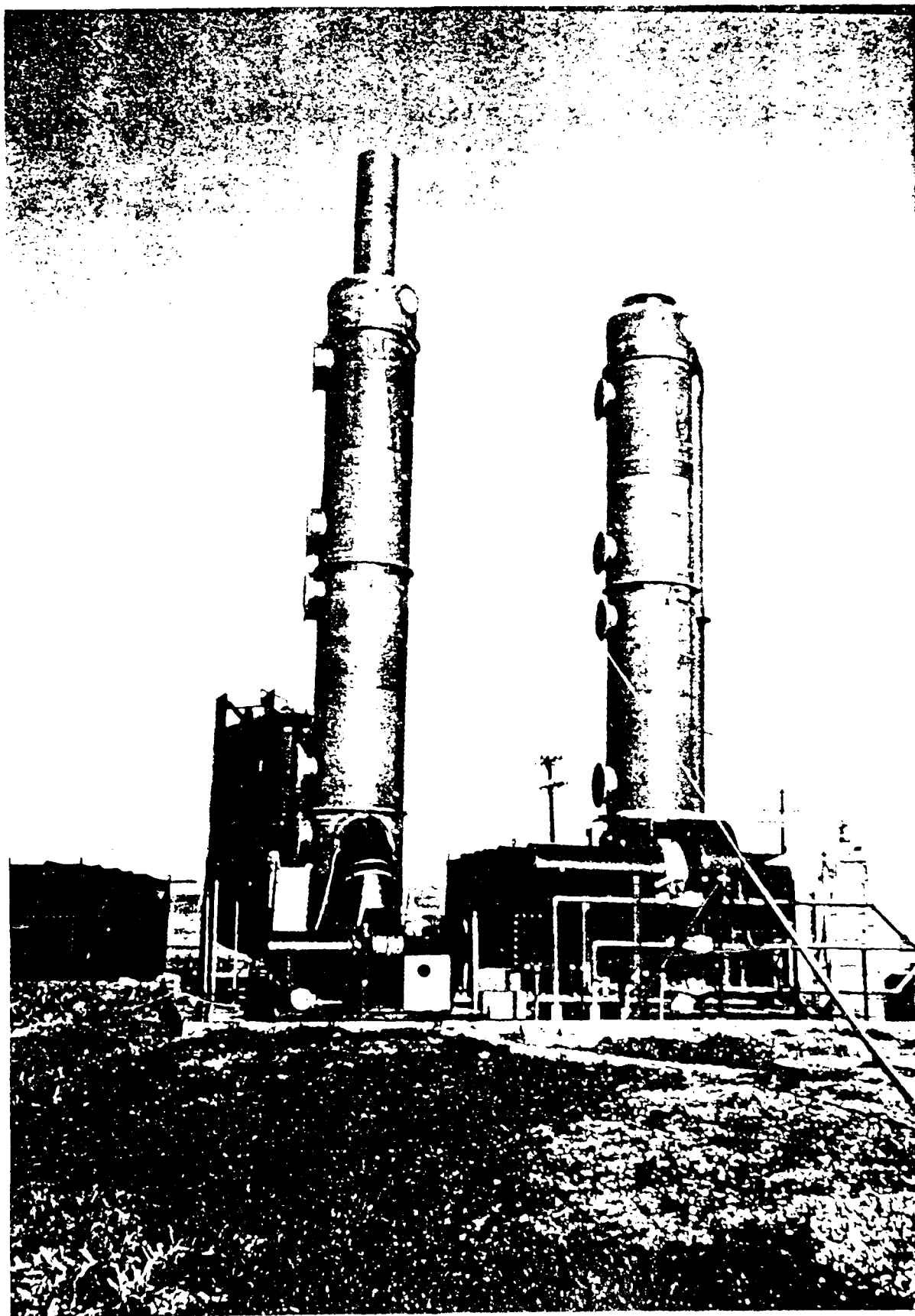
Figure 3 is a photograph of the treatment site at LEAD before it was enclosed in a weatherized building. Figure 4 is a process flowsheet of the site. Two 4-foot diameter towers made of fiberglass-reinforced plastic were constructed with each tower containing 20 feet of 3.5-inch Jaeger tri-pack poly packing. Initially, three 200-foot deep recovery wells (R1, R2, and R3) were used as groundwater monitoring points. Each extraction well recovery system was installed using schedule 80 PVC piping which was laid in a 48-inch-deep trench. Direct routing of the three separate lines was selected to pump and control each well independently. Each well was equipped with flow totalizers and valves for flow adjustments. The well connections were 2 inches in diameter with the line sizes increasing to 3 inches in diameter approaching the treatment site.

About one year after the treatment site began operations, seven additional wells were installed at the facility. These additional wells increased the pumping capacity of the site from 80 gal/min to 200 gal/min.

Prior to treatment the water is filtered through three 50-micrometer bag filters rated at 150 pounds/square inch (lb/in²) to remove suspended solids and preclude fouling of the tower packing or blinding of the final absorber. A 2,000-gallon polyethylene equalization tank is used for blending the groundwater prior to air stripping. This tank also serves as a holding tank to prevent the recovery wells from being pumped dry. The well pumps, if operated continuously around-the-clock, will pump the underground watertable dry. Therefore, the well pumps are operated on an intermittent basis to fill the holding tank. Once this is accomplished, the pumps are shut down until the tank is empty and needs refilling. The tank is equipped with high- and low-level switches which activate the pumps at the recovery wells. The same type of level control system is also employed on the sump of both air strippers.



Figure 3
VOC Water Treatment Plant Letterkenny Army Depot



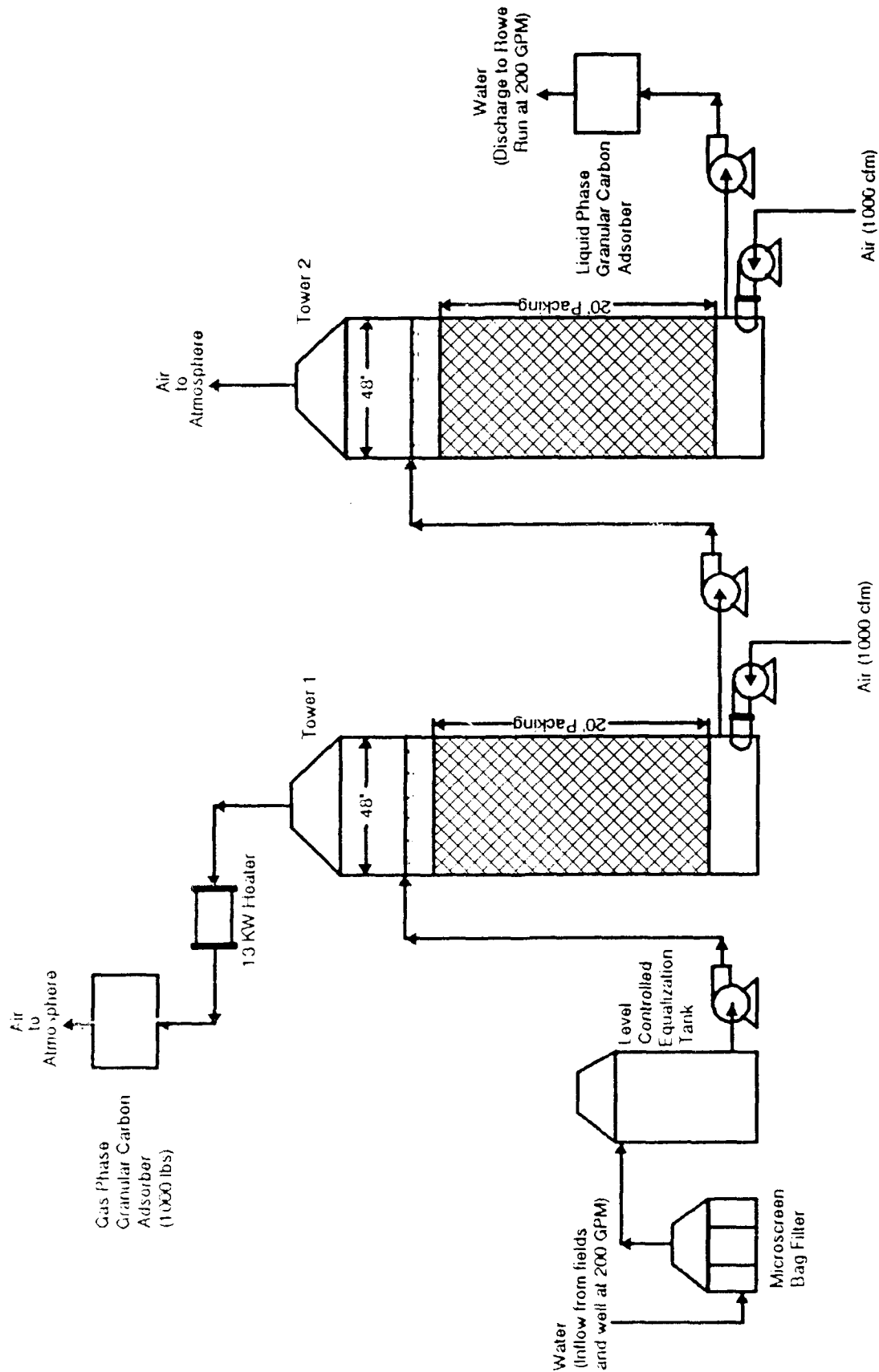


Figure 4
Flowsheet of Water Treatment Plant at Letterkenny Army Depot

The 4-foot-diameter air strippers operate in series. As the water leaves the second air stripper, it is further cleaned in a 10,000-pound, liquid-phase granular carbon absorber. The liquid-phase carbon absorber is included to remove possible nonvolatile organics from the water. It was not fully known at the time the plant was designed what type of nonvolatile organics were in the groundwater; therefore, the aqueous-phase carbon absorber was included in the design to provide additional treatment to the water as it exits the second air stripper. The water is then discharged through a 4-inch line into a nearby creek about 130 feet from the facility. Two air blowers (one/tower) are used to strip the VOCs from the water as it is pumped through the towers. Each air blower pushes about 1,000 ft³/min through each tower. Design modeling and actual data have shown that more than 99 percent of the influent VOCs are removed by the first air stripper.

The high concentration of VOCs in the exit air stream from the first air stripper is treated by passing heated off-gas through a 10,000-pound vapor-phase carbon absorber. A 13-kilowatt (kW) heater is used to reduce humidity to less than 50 percent. Two parallel absorbers are installed to allow immediate switching to a fresh carbon bed when the online carbon is spent. Removal of the remaining VOCs by the second tower operating at a high air:water ratio will not produce significant stack emissions; therefore, no vapor-phase carbon emission system is judged necessary for this tower.

Sharpe Army Depot (SHAD)

SHAD is located in Lathrop, California. It provided maintenance services for vehicles, aircraft, and industrial and medical equipment from 1941 to 1975. Organic solvents were used in these operations for degreasing, paint stripping, and paint spraying. Spent solvents and sludge from these operations were land applied. A 1981 environmental survey of SHAD determined that the contamination levels in groundwater exiting the depot exceeded acceptable criteria. Sampling studies at this time verified that the volatile organic contamination originated in the South Balloon area at the southernmost portion of the depot. Additionally, contamination in an area known as the North Balloon area has also been found at the northernmost portion of the depot. Both the South Balloon and North Balloon areas were targets for air-stripping towers to be built for use in decontaminating the groundwater.

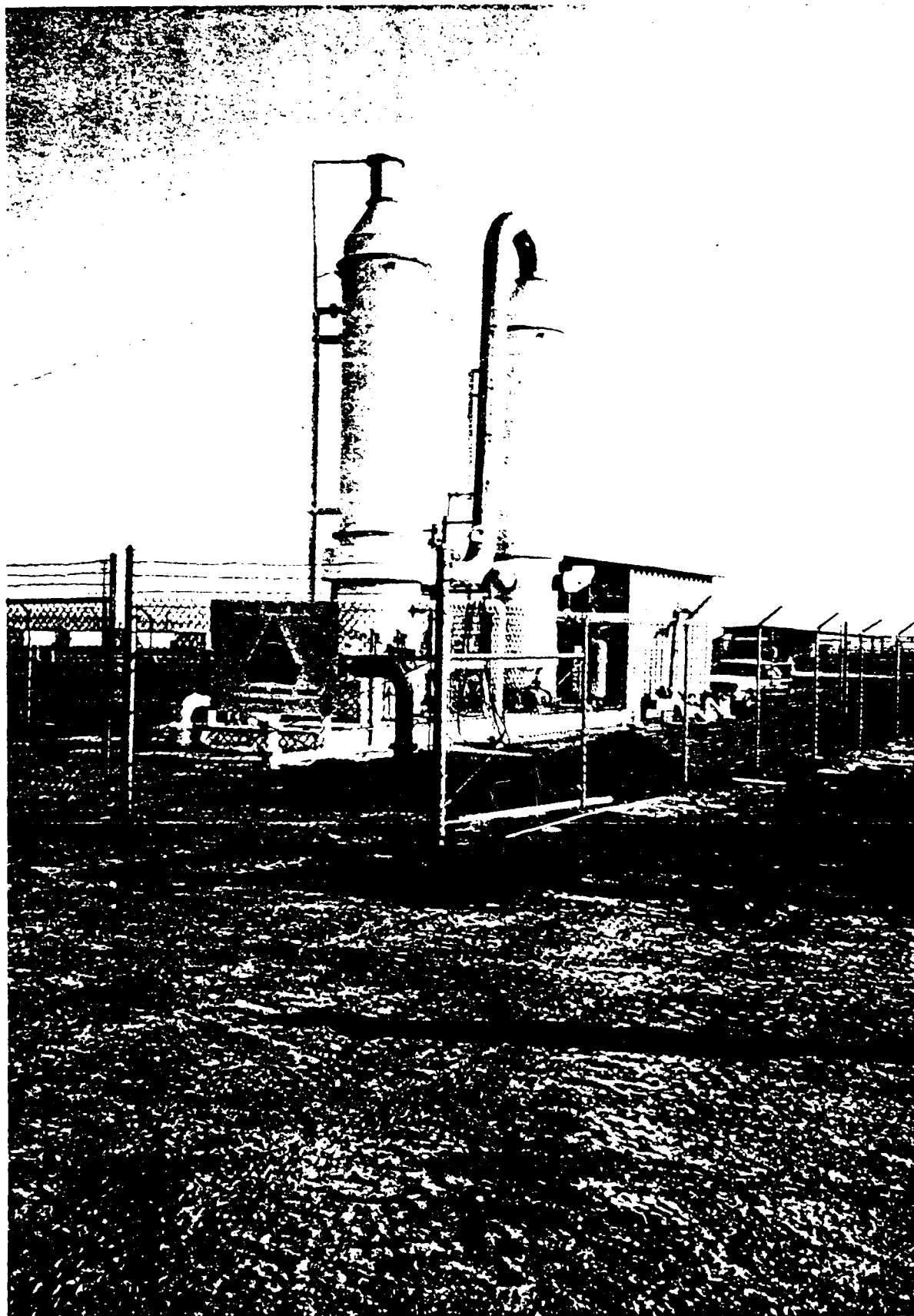
An analysis of the groundwater at SHAD shows that it was contaminated with the following three major contaminants:

<u>Influent</u>	<u>Concentration, µg/L</u>
cis-1,2-dichloroethylene	20
Chloroform	3
Trichloroethylene	190

A packed-column air-stripping water treatment plant was constructed at SHAD to remediate the VOCs from the underground water aquifers.

Figure 5 is a photograph of the South Balloon treatment plant. Figure 6 is a flowsheet of the process used to treat the groundwater at SHAD; the dimensions are based on the North Balloon site.

Figure 3
VOC Water Treatment Plant at Sharpe Army Depot



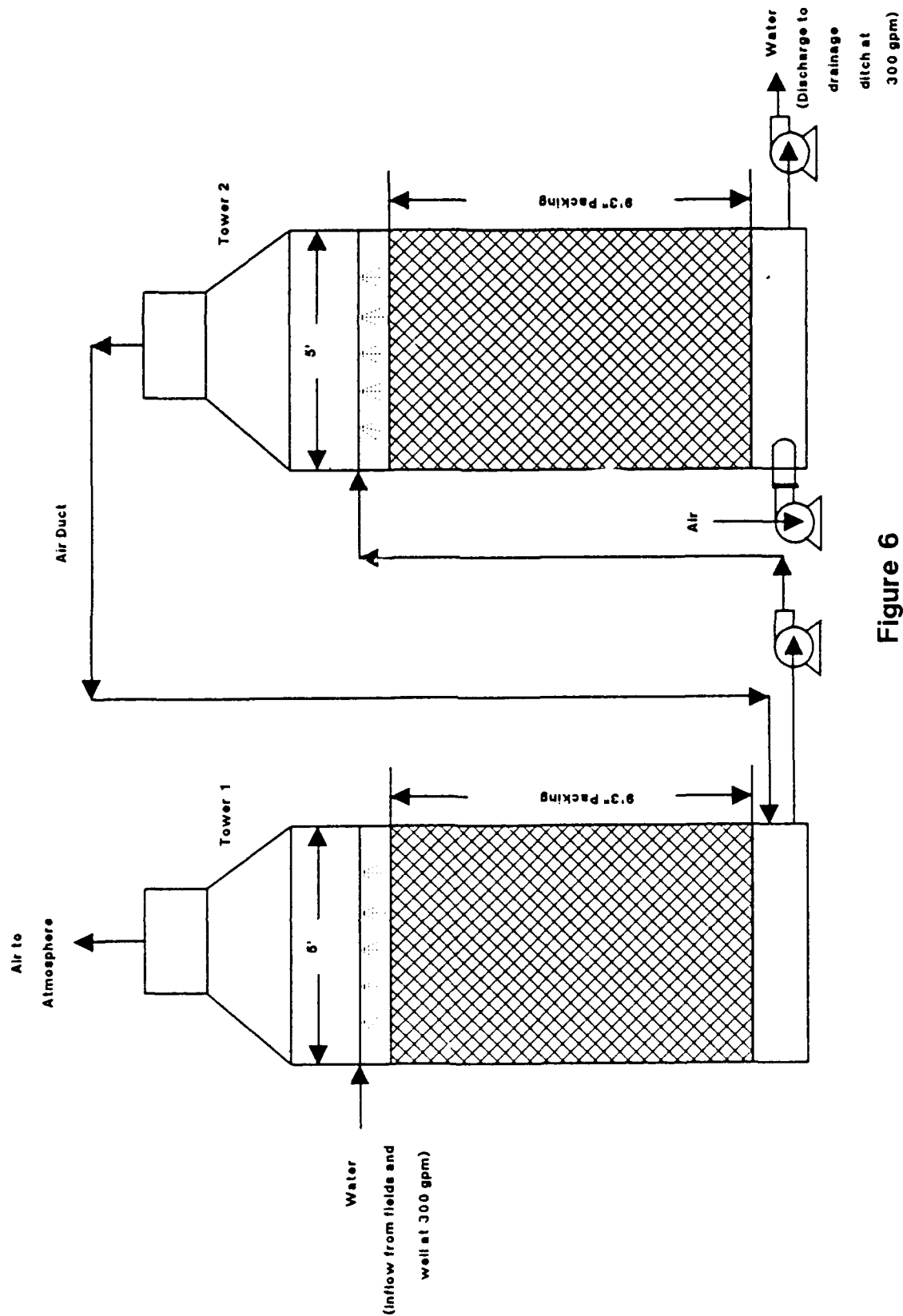


Figure 6

Flowsheet of Water Treatment Plant at Sharpe Army Depot

The North Balloon site at SHAD consists of two towers in series, operating continuously around the clock to process approximately 300 gal/min of water. Because of the warm climate, the treatment plant does not require an enclosed building. The control room is enclosed to protect the electronic and data-gathering equipment from the weather. The two towers are 60 inches in diameter and are constructed of fiberglass-reinforced plastic. The packing height in each tower is 9.25 feet for a total packing volume of 360 cubic feet (ft³). The packing used in each tower is Cascade No. 1-A plastic 1-inch mini ring. The towers are operated in series so that the water is processed through one tower and then through the second tower before being discharged through an 8-inch-diameter pipe to a storm drain.

The plant currently operates using just one blower which moves air at a rate of about 3,000 ft³/min. The air enters below the bottom of the packing level of the first tower, passes upward through the tower, and exits out the top of the first tower through a duct. The duct transfers the air below the bottom of the packing level of the second tower and then out the top of the second tower into the atmosphere. The plant operates at an air:water ratio of 75:1.

The water is pumped into the water treatment site from a series of boundary wells and source control wells located around the plant area. There are currently 15 boundary wells. Each well has its own pump. All of the wells pump the water into a single eight-inch pipe system. The piping coming off the well is galvanized steel. PVC pipe is used for most of the forcemain system, especially where it is laid in underground trenches before reaching the treatment site. Most of the plant piping is also PVC, although there is some carbon steel pipe which is used for transferring the water within the plant area.

ECONOMIC EVALUATION

Capital Costs

The capital costs for each of the facilities, all extraction wells, and the forcemain collection systems were taken from contract documents, bid documents, construction cost reports, and other data obtained at each site and/or from USATHAMA. The costs were collected and categorized according to the listings in the following paragraphs.

The costs shown for extraction and monitoring wells include well drilling, casings, pump and piping in the well, and the well head. The forcemain system includes costs for wellhouses, excavations, piping and valves to collect the water, backfill of trenches, road crossings, and site cleanup.

The cost figures presented in this report are broken down into the following categories:

- Construction Costs - These costs represent the total expenditures for materials and equipment and installation labor required to build and place in operation the air-stripping facility, the

collection wells, and the forcemain system. The forcemain system cost also includes the pump and/or wellhouse costs. In each case, this work was accomplished by various subcontractors working for a general contractor. Generally the costs are for foundations, buildings, process equipment, electrical systems and instrumentation control, piping, and for mechanical systems.

- **Startup Expense** - This amount covers the costs of material and labor required to get the plant and equipment operating at full design capacity. It includes costs for mobilization of equipment and on site setup by the general contractor. Decontamination of equipment is also in this category.
- **Health and Safety** - These costs are for medical surveillance of workers during and after construction due to handling of contaminated materials. The general contractor also included costs for the implementation of his workers' health and safety plan.
- **Overhead and Profit** - These costs are for the contractor's company overhead, employee benefits, and for the profit earned for completing the work required under the contract.
- **Engineering** - The engineering costs associated with these construction projects include all costs for the engineering salaries, travel, per diem, office expense, etc., for design of the air-stripping facility, wells, and forcemain system. Also included in this category are the costs for reviewing bids, awarding contracts, monitoring construction, and assisting operators during the startup of the plant.
- **Project Management** - These costs include all charges (salaries, benefits, travel, per diem, office expenses, etc.) that are normally associated with the overall responsibility of a construction project. For these air-stripping projects, these charges cover risk assessment, monitoring and coordinating other engineering contracts, monitoring performance of work, and overseeing operations and maintenance during the startup and testing of the plant. This category also covers costs for report writing and final recordkeeping.
- **Disposal of Waste** - These costs are for collecting and disposing of waste materials generated during construction. This includes filters and filter media, gloves, clothing, chemicals, and other contaminated materials.

Care should be used when comparing the capital costs of one facility with another due to considerable differences in design, geographical location, capacity, and method of operation.

Operating and Maintenance Costs

Where possible, the maintenance costs were determined from existing maintenance contracts such as TCAAP and SHAD. At LEAD, the costs were determined based on discussion with plant operators and maintenance personnel. The facilities selected for study do not have a person(s)



dedicated totally to the plant. Therefore, personnel costs for operators were sometimes estimated as explained in the discussion for each site. Utility costs are included here.

Total Life-Cycle Cost

The total life-cycle cost (TLCC) for each facility was calculated using the guidelines of NBS Handbook #135 published for the Department of Energy. This handbook provides procedures and formats to calculate the cost effectiveness of new system designs. All existing cost data was converted to base dollars and the life of the plant was assumed to be 30 years.

The Uniform Present Worth (UPW) and the Single Plant Worth (SPW) discount factors are taken from the tables in the NBS Handbook #135. The ten-percent discount rate is defined for Federal use to be "real" rates exclusive of general price inflation. The factors are applied as multipliers to future amounts which are stated in "constant" dollars--that is, exclusive of general price inflation.

Significant Cost Drivers

The significant cost drivers--individual cost items that have an impact on capital or operating cost--were determined from the capital cost information explained above, the calculated costs of utilities, and from operations and maintenance contracts. In the discussion for each facility, the significant drivers are identified and listed in individual tables.

Twin Cities Army Ammunition Plant (TCAAP)

The total capital investment for the existing TCAAP facility as constructed is summarized in Table 1. The costs include all direct and indirect charges normally associated with a capital construction project (material, labor, startup, overheads, profit, project management, and engineering). This table shows the installed costs for the treatment plant, extraction wells, and a forcemain collection system with necessary pumphouses (in 1990 dollars). The 2,900 gal/min treatment plant as described in the process review was built adjacent to an existing water plant and used one wall as a common wall. This groundwater remediation project was completed in phases and involved different construction companies working over a long period of time resulting in higher costs due to additional mobilization/demobilization expenses, additional health and safety plans, etc.

The cost information obtained at TCAAP indicates that a total of 81 wells were installed throughout the facility. This includes 16 extraction wells, 17 return wells, and 48 monitoring wells. These wells vary in depth, diameter, and underground water flow rate. Sixteen of the wells have pumphouses installed over them for freeze protection. A complete hydrological survey was conducted to determine necessary information for well drilling. The cost of this survey is in the engineering costs for "wells" shown in Table 1.

The cost of the forcemain system and pumphouses includes approximately 17,800 linear feet of ductile iron pipe, 16 pumphouses, 16 return well structures, and other valves and controls. The pipe is installed in trenches a minimum of 7 feet below grade and ranges in size from 6 to 16 inches in diameter. Pumphouse costs include structures, pumps, controls, all electrical and mechanical systems, and controls to tie the wells to the forcemain system.

Table 1

Twin Cities Army Ammunition Plant
New Brighton, Minnesota

Capital Costs (1990 \$)

<u>Category</u>	<u>Treatment Plant</u>	<u>Wells</u>	<u>Forcemain & Pumphouses</u>	<u>Total</u>
Construction Cost	\$ 774,757	\$1,026,406	\$2,386,712	\$4,187,875
Startup	135,930	71,861	150,429	358,220
Health and Safety	21,150	41,748	47,227	110,125
Overhead and Profit	236,225	245,889	392,143	874,257
Engineering	449,769	546,738	579,203	1,575,710
Project Management	<u>319,862</u>	<u>331,523</u>	<u>276,882</u>	<u>928,267</u>
Total Capital Cost	\$1,937,693	\$2,264,165	\$3,832,596	\$8,034,454

Table 2 shows the annual operating costs for the existing TCAAP facility. The actual operating and maintenance costs were obtained from TCAAP (Alliant Tech Systems) for the calendar year 1990. This includes all personnel costs, overheads, materials, field purchases, and lab expenses. The capacity of the TCAAP facility is approximately 2,900 gal/min (1.524×10^9 gallons/year) of treated water. The utility cost for the air-stripping facility is for electricity only. A monthly breakdown of electrical usage was provided upon request and was used to calculate electrical cost. Total kWh at \$0.0425/kWh was 1,739,561 (\$73,931.34). Total kWh at \$0.0443/kWh was 1,691,087 (\$74,915.15). Total cost for electricity was \$148,846.49. Monthly usage and cost is shown on Table 3. (Note: The utility rate increased in July 1990 from \$0.0425/kWh to \$0.0443/kWh).

Table 4 shows the total life-cycle cost calculations for the TCAAP facility. The costs shown represent the TLCC and the annual operating cost expressed in 1,000 gallons of water treated. The TLCC is equal to \$0.2971/1,000 gallons whereas the total cost of operation and maintenance only (i.e., TLCC - capital cost) is equal to \$0.1214/1,000 gallons.

Table 2

Twin Cities Army Ammunition Plant
New Brighton, Minnesota

Annual Operating Costs

<u>Cost Item:</u>	<u>Annual Cost (1990 \$)</u>
• Utilities	\$148,846
• Professional Services	219,502
• Maintenance	150,054
• Lab Charges	25,175
• Other O&M Costs	<u>39,518</u>
 Total	 \$583,095
• Non-Annual Recurring (Non-Fuel) Costs Every Fifth Year - Tower Packing	 \$ 20,865

Table 3

Twin Cities Army Ammunition Plant
New Brighton, Minnesota

Annual Power Usage and Cost

<u>Month</u>	<u>Kilowatt Hours</u>			<u>Power Cost (\$)</u>	<u>Total Electrical Cost (\$)</u>
	<u>Wells</u>	<u>Treatment</u>	<u>Total</u>		
01/90	237,348	89,040	326,388	\$0.0425/kWh	\$13,871.49
02/90	195,170	85,200	280,370	\$0.0425/kWh	11,915.73
03/90	202,320	90,840	292,847	\$0.0425/kWh	12,446.00
04/90	179,336	83,280	262,616	\$0.0425/kWh	11,161.18
05/90	185,709	88,080	273,789	\$0.0425/kWh	11,636.03
06/90	203,711	99,840	303,551	\$0.0425/kWh	12,900.92
07/90	162,960	78,960	241,920	\$0.0443/kWh	10,717.06
08/90	158,751	88,320	247,071	\$0.0443/kWh	10,945.25
09/90	213,979	92,280	306,259	\$0.0443/kWh	13,567.27
10/90	191,556	89,520	281,076	\$0.0443/kWh	12,451.67
11/90	205,976	87,240	293,216	\$0.0443/kWh	12,989.47
12/90	230,345	91,200	321,545	\$0.0443/kWh	14,244.44

Table 4

Twin Cities Army Ammunition Plant
New Brighton, Minnesota

Total Life-Cycle Cost

	<u>Present Value</u>		
1. Capital Cost - Total Investment	\$ 8,034,454		
2. Annual Energy Cost (\$148,846.49 x 9.58) 9.58 = UPW Discount Factor	1,425,949		
3. Annual (Non-Fuel) O&M Cost (\$434,249 x 9.43) 9.43 = UPW Discount Factor	4,094,968		
4. Non-Annual Recurring (Non-Fuel) O&M Cost	31,089		
<u>Year</u>	<u>Amount</u>	<u>SPW Factor</u>	<u>Cost</u>
5th	\$20,865	.62	\$12,936
10th	20,865	.39	8,137
15th	20,865	.24	5,008
20th	20,865	.15	3,130
25th	20,865	.09	<u>1,878</u>
			\$31,089
Total Life-Cycle Cost			<u><u>\$13,586,460</u></u>

Capital Cost/1,000 gal = .1757
(TLCC-opn costs)

Opn/1,000 gal = .1214
(TLCC-capital cost)

TLCC/1,000 gal = \$.2971

One additional cost item is the replacement of tower packing. To date, no packing has been replaced. TVA's engineering estimate indicates one third of the tower packing should be replaced every five years ($1/3 \times 4,500 \text{ ft}^3 = 1,500 \text{ ft}^3 \times \$13.91/\text{ft}^3 = \$20,865$). This will account for the normal wear, settling, and fouling of the packing material. The cost for tower packing was taken from the capital cost report obtained at TCAAP. The replacement of tower packing is considered a non-annual, recurring (non-fuel) operating and maintenance (O&M) cost and is shown in Table 4.



Table 5 shows significant cost drivers for the existing TCAAP facility. These costs shown are direct construction costs only and do not include engineering and project management costs.

Table 5

Twin Cities Army Ammunition Plant
New Brighton, Minnesota

Significant Cost Drivers

<u>Capital Costs:</u>	<u>(1990 \$)</u>
• Process Equipment	
- Stripping Towers	\$296,821
- Transfer Pumps	47,880
• Wet Wells	142,740
• Enclosure	64,855
• Extraction Monitor and Return Wells (81)	
- Well Drilling (Approximately 16,750')	399,633
- Well Casings	241,095
• Pump Houses	775,904
- 6 @ \$48,134	
- 10 @ \$48,716	
 <u>Annual Operating Costs:</u>	
• Utilities	\$148,846
• Professional Services	219,502
• Subcontracted Maintenance Repairs	150,054

Letterkenny Army Depot (LEAD)

The total capital investment for the existing LEAD facility as constructed, is summarized in Table 6. The costs include all direct and indirect charges as described in previous sections of this report. The cost data received from LEAD was the March 1989 contract pricing proposal from Hunter/ESE, the primary contractor for design and construction of the facility. The design included an insulated metal building with a complete heating system to prevent freezing in the winter. Although this facility was designed to treat approximately 200 gal/min, the cost information contained in this report is for three extraction wells that only produce 80 gal/min. Four monitoring wells were also installed

Table 6

Letterkenny Army Depot
Chambersburg, Pennsylvania

Capital Costs (1990 \$)

<u>Category</u>	<u>Plant</u>	<u>Wells</u> ⁴	<u>Forcemain</u> ²	<u>Total</u>
Construction Cost	\$ 248,735 ¹	\$ 209,738		\$ 458,473
Startup	344,775 ⁵			344,775
Health and Safety ³				
Overhead and Profit	73,322	28,628		101,950
Engineering	326,141	220,530		546,671
Project Management	<u>57,965</u>	<u>31,211</u>		<u>89,176</u>
Total Capital Investment	\$1,050,938	\$ 490,107		\$1,541,045
Total Estimated Value of Seven Additional Wells	<u> </u>	<u>513,100</u>		<u>513,100</u>
Estimated Capital Investment	\$1,050,938	\$1,003,207		\$2,054,145

¹ Includes mobile Aquifier Test Treatment Unit (\$61,100).

² Included with plant cost.

³ Not listed as a separate cost.

⁴ Costs for three initial extraction wells. Seven added later, cost not available.

⁵ Includes operating costs (six months) for startup (\$247,000).



in the original design. Seven additional extraction wells have since been installed but the cost information has not been made available for inclusion in this writing. Based on the costs for the three extraction wells initially installed, the total costs for seven more would be approximately \$513,100 or an estimated value of \$73,300 each. This additional capital cost will bring the estimated value of the installed system to \$2,054,145.

At LEAD's facility, the small costs for the forcemain collection system are included with the cost of the treatment plant. This system consists of approximately 400 feet of one-inch CPVC piping buried a minimum of 48 inches below grade. No pumphouses or wellhouses were necessary for freeze protection due to pumps and piping underground. Because of the closeness of the three wells to the treatment facilities, the piping costs of the forcemain collection system are not significant to this project. The costs for the hydrological survey are included in the engineering costs for the wells.

The annual operating costs are shown in Table 7 and include the electrical costs, operators, maintenance costs, and replacement of carbon for the absorbers. The electrical usage is metered at the treatment site. Since the plant has not been in operation for a year, the total annual consumption was estimated based on the latest information obtained from LEAD through December 1990. The electrical costs include ten well pumps operating as explained earlier. The charges for electricity at the present rate of \$0.0350 per kilowatt-hour is \$2.72 per hour. This calculates to be \$23,827 on an annual basis.

According to Peters and Timmerhaus, Plant Design and Economics for Chemical Engineers, Third Edition, maintenance contracts for this type of operation generally run about two to six percent of the total capital investment. Without a maintenance contract in place, the maintenance costs have been estimated to be \$58,230 per year. This amount has been used in Table 7 to represent a maintenance cost of approximately 2.8 percent of the total capital investment.

An additional cost item to be included in the total operating and maintenance costs is the replacement of tower packing every five years. One third of the total volume will be required to be replaced at a cost of \$2,968 ($1/3 \times 503 \text{ ft}^3 = 168 \text{ ft}^3 \times \$17.70/\text{ft}^3 = \$2,968$). This replacement is indicated in Table 7, Annual Operating Cost, and Table 8 which shows the total life-cycle cost calculations for the LEAD facility. The costs are representative of the TLCC and the annual operating cost is expressed in 1,000 gallons of water treated.

The TLCC is equal to \$1.3185/1,000 gallons with the carbon absorption units and \$0.8814/1,000 gallons without the carbon units. The operating costs calculate to be \$0.6671/1,000 gallons with the carbon units and only \$0.2712/1,000 gallons without the carbon units.

Table 9 shows the significant cost drivers for the existing facility. These costs are construction costs only and do not include engineering, project management, or other indirect costs. The installation at LEAD is more complex in that the Pennsylvania Department of Environmental Resources (PADER) requires that a carbon absorption system be installed in addition to the air stripping towers. The capital costs shown in Table 6 includes both gas and liquid carbon absorption units.



Table 7

Letterkenny Army Depot
Chambersburg, Pennsylvania

Annual Operating Costs

<u>Cost Item:</u>	<u>Annual Cost (1990 \$)</u>
• Operating Personnel	\$ 7,621
• Utilities	23,827
• Maintenance	58,230
• Carbon	132,400
• Non-Annual Recurring (Non-Fuel) Cost Every Fifth Year	\$ 2,968

Table 8

Letterkenny Army Depot
Chambersburg, Pennsylvania

Total Life-Cycle Cost

	<u>Present Value</u>
1. Capital Cost - Total Investment (with carbon absorbers)	\$ 2,054,145
2. Annual Energy Cost (\$23,827 x 9.65) 9.65 = UPW Discount Factor	229,931
3. Annual Recurring (Non-Fuel) O&M Cost (\$198,251 x 9.43) 9.43 = UPW Discount Factor	1,869,507
4. Non-Annual Recurring (Non-Fuel) O&M Cost	4,422

<u>Year</u>	<u>Amount</u>	<u>SPW Factor</u>	<u>Cost</u>	
5th	\$ 2,968	.62	\$ 1,840	
10th	2,968	.39	1,158	
15th	2,968	.24	712	
20th	2,968	.15	445	
25th	2,968	.09	267	
			\$ 4,422	
			Total Life-Cycle Cost	\$ 4,158,005

	<u>With Carbon Absorbers</u>	<u>Without Carbon Absorbers</u>
Capital Cost/1,000 gal = (TLCC - opn costs)	\$.6514	\$.6102
Opn/1,000 gal = (TLCC - capital cost)	\$.6671	\$.2712
TLCC/1,000 gal)	\$1.3185	\$.8814



Table 9

Letterkenny Army Depot
Chambersburg, Pennsylvania

Significant Cost Drivers

<u>Capital Costs:</u>	<u>(1990 \$)</u>
• Process Equipment	
- Stripping Towers	\$ 34,712
- Carbon Absorbers	84,310
• Metal Building	27,100
• Extraction and Monitoring Wells (7)	209,738
• Seven Additional Extraction Wells	232,700
 <u>Annual Operating Costs:</u>	
• Carbon Replacement	\$132,400
• Maintenance	58,230

Sharpe Army Depot (SHAD) Economic Evaluation

The total capital investment for the existing SHAD facility as constructed in the North Balloon Area is summarized in Table 10. These costs include all direct and indirect charges as explained in previous sections of this report. The North Balloon Area treatment facility at SHAD will process 300 gal/min and uses a storm drain to dispose of the treated water. The treatment facility does not have nor does it need any freeze protection as does the plants at TCAAP and LEAD. The cost information in Table 11 is for the treatment plant, the extraction wells, and the forcemain collection system and represents a one-time expenditure for design and construction.

The capital cost information obtained from SHAD indicates that 14 extraction wells were drilled and cased in the original North Balloon Area facility. In 1990, one additional well was drilled and connected to the North Balloon treatment facility. The costs shown in Table 11 reflect this addition and were included with the original construction cost. Due to the mild climate in California, none of the well sites required a pumphouse to be constructed to protect them. Each wellhead was protected by steel posts set in concrete that serve as a traffic barrier.

The forcemain collection system consists of approximately 3,880 feet of underground PVC pipe ranging in size from one inch in diameter to six inches in diameter and is buried a minimum of three feet below the surface.

Table 10

Sharpe Army Depot - North Balloon Area
Lathrop, California

Capital Costs (1990 \$)

<u>Category</u>	<u>Plant</u>	<u>Wells</u>	<u>Forcemain</u>	<u>Total</u>
Construction Cost	\$ 236,223	\$ 353,588	\$ 129,789	\$ 719,600
Startup	16,132	21,562	8,881	46,575
Health and Safety	52,480	68,382	28,834	149,696
Overhead and Profit	59,056	96,824	32,447	188,327
Engineering	62,556	95,800	28,947	187,303
Project Management	30,224	39,382	16,606	86,212
Disposal of Waste	<u>2,200</u>	<u>3,250</u>	<u> </u>	<u>5,450</u>
Total Capital Cost	\$ 458,871	\$ 678,788	245,504	\$1,383,163

The actual operating and maintenance costs were taken from a firm, fixed-price maintenance contract between SHAD and Calcon Systems, Inc., San Ramon, California. The cost breakdown for this contract is for preventative maintenance, calibration, service, and repairs. This fixed-price contract was for the VOC air-stripping facility at Sharpe Army Depot that is in operation now (South Balloon area). This plant is designed and operated nearly identical to the facility constructed in the North Balloon Area. For this report, the operating and maintenance costs for the South Balloon plant have been used to project the expected costs for the North Balloon plant.

The utility costs for the North Balloon plant was also determined from the air-stripping unit for the South Balloon Area. The utility records show 250,308 kWh of electricity was used at this plant site. The current rate for electricity for the Lathrop, California region is \$0.0387 per kilowatt hour. This cost calculates to be \$9,687 per year. Electricity is the only utility cost included in the operation of the plant. The annual operating costs are summarized in Table 11.

Table 11

Sharpe Army Depot - North Balloon Area
Lathrop, California

Annual Operating Costs

<u>Cost Item</u>	<u>Annual Cost</u>
• Utilities	\$ 9,687
• Maintenance ¹	23,352
• Inspection Services ¹	26,880
• Parts, Material, and Equipment Rental ¹	<u>15,000</u>
	\$74,919

¹Items listed on maintenance contract.



An additional cost item to be included in the total operating and maintenance costs is the replacement of tower packing every five years. Approximately one third of the total volume of tower packing will be required to be replaced every five years at a cost of \$2,096. This is equivalent to 121 cubic feet of packing ($1/3 \times 363 \text{ ft}^3 = 121 \text{ ft}^3 \times \$17.32/\text{ft}^3 = \$2,096$). This replacement is shown in Table 12 showing the total life-cycle cost for the facility. The costs shown in this table are representative of the TLCC and the annual operating costs expressed in 1,000 gallons of water treated. The TLCC is equal to \$0.4442/1,000 gallons and the annual operating cost is equal to \$0.1518/1,000 gallons of treated water.

Table 12

Sharpe Army Depot - North Balloon Area
Lathrop, California

Total Life-Cycle Cost

				<u>Present Value</u>
1.	Capital Cost - Total Investment			\$ 1,383,163
2.	Annual Energy Cost (\$9,687 x 10.31) 10.31 = UPW Discount Factor			99,873
3.	Annual O&M Cost (\$65,232 x 9.43) 9.43 = UPW Discount Factor			615,138
4.	Non-Annual Recurring (Non-Fuel) O&M Cost (Replacement of packing)			3,123
	<u>Year</u>	<u>Amount</u>	<u>SPW Factor</u>	<u>Cost</u>
	5th	\$ 2,096	.62	\$1,300
	10th	2,096	.39	817
	15th	2,096	.24	503
	20th	2,096	.15	314
	25th	2,096	.09	189
				<u>\$3,123</u>
				<u><u>\$ 2,101,297</u></u>
			Total Life-Cycle Cost	

Capital Cost/1,000 gal = \$.2924
(TLCC - opn cost)

Open Cost/1,000 gal = \$.1518
(TLCC - capital cost)

TLCC/1,000 gal = \$.4442



Table 13 shows the significant cost drivers for the North Balloon Area treatment facility. The costs shown are construction costs only and do not reflect costs for engineering or project management.

Table 13

Sharpe Army Depot - North Balloon Area
Lathrop, California

Significant Cost Drivers

<u>Capital Costs</u>	<u>(1990 \$)</u>
• Process Equipment	
- Stripping Towers	\$ 64,588
• Extraction and Monitoring Wells	
- Well Pumps	29,925
- Pump Control Panels	56,430
- Well Drilling and Casing	95,162
• Forcemain Collection System	
- Railroad Track Crossing (Borings)	54,577
<u>Annual Operating Costs</u>	
• Labor (Maintenance) ¹	23,352
• Weekly Inspections and Reports ¹	21,840

¹ Item listed on maintenance contract.

SUMMARY

Shown in Table 14 is the total life-cycle cost (TLCC) (including capital costs) and the operating costs (excluding capital charges) per 1000 gallons of water treated for the three sites. With each site having varying capacity, the potential for economy of scale can be seen. Although the designs for each plant are not identical, there is a reasonable correlation that can be used for projecting approximate future costs.

Table 14

<u>Plant</u>	<u>Flow, GPM</u>	<u>Capital, \$</u>	<u>Operating \$/1,000 gal</u>	<u>TLCC \$/1,000 gal</u>
TCAAP	2,900	8,034,454	.1214	.2971
LEAD	200	2,054,145	.6671	1.3185
SHAD	300	1,383,163	.1518	.4442



The operating costs per 1,000 gallons shown above was calculated using the annual operating cost discounted over the 30-year life of the plant.

For the LEAD facility, the use of carbon adsorption completely overshadowed any cost associated with the basic air-stripping process. If the carbon absorbers were not required, the operating costs would be approximately \$.27 per 1,000 gallons.

The most significant cost drivers for the basic air-stripping operation were found to be the following:

- Air Stripping Tower Capital Cost
- Utilities
- Maintenance Contracts
- Carbon Absorbers (LEAD)

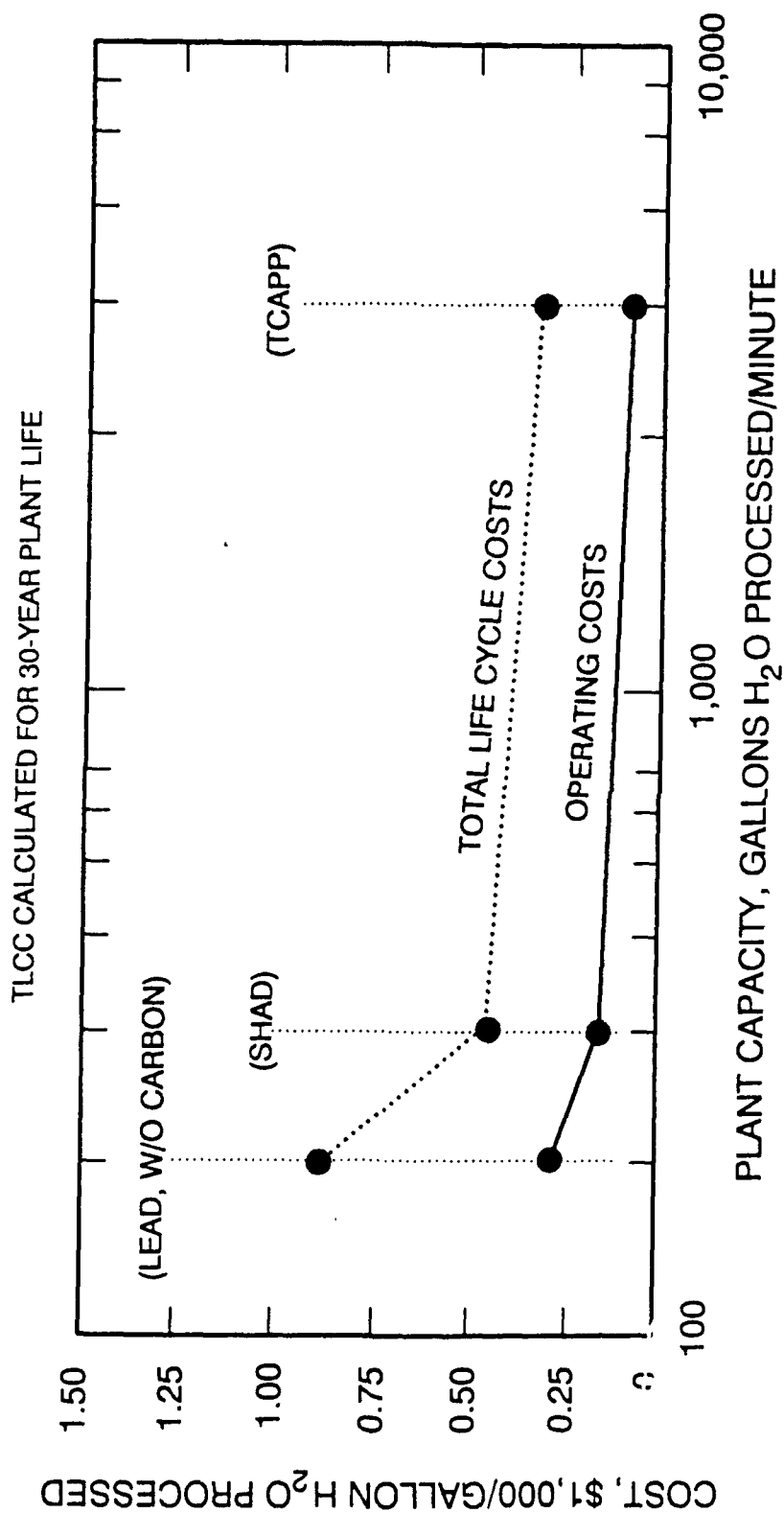
The following graph indicates an economy of scale in both total life cycle costs and operating costs based on costs per 1,000 gallons of treated water. The graph is made from data shown in Table 14.

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of this report, the following conclusions and recommendations can be made in the use of air stripping to remove VOCs from groundwater.

- Several variables will affect tower design for an air stripping unit. These include the liquid flow rate through the tower, water temperature, contaminant concentration in the influent water supply, desired effluent contaminant concentration, air:water mass ratio, characteristics of tower packing, and the height of the packing/tower.
- Because of the concentration levels of the contaminants in the water at LEAD and due to existing environmental regulations on emissions, carbon adsorption is required on the effluent water and the exit air from the first tower operating series.
- Because of the vast differences in design parameters and methods of operation, the plants should not be directly compared with each other based on costs alone.
- An independent organization should review site assessments, design layouts, and bid proposals before contracts are awarded for new facilities. Also, construction, startup, and operation should be better monitored to provide USATHAMA with more complete and timely operating and cost information for each site.

COST OF AIR STRIPPING VERSUS PLANT CAPACITY



- There is economy of scale in that the operating cost per 1,000 gallons of treated water declines as the flow rate increases.
- A consistent format should be used to record and report costs and operating data.
- Except for the costs of LEAD, the reported TLCC and operating costs are within the ranges published in Environmental Science Technology, Vol. 22, No. 10, 1988.

